

Quantum Statistical Mechanics. IV. Non-Equilibrium Probability Operator and Stochastic, Dissipative Schrödinger Equation

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The probability operator for a generic non-equilibrium quantum system is derived. The corresponding stochastic, dissipative Schrödinger equation is also given. The dissipative and stochastic propagators are linked by the fluctuation-dissipation theorem that is derived from the unitary condition on the time propagator. The dissipative propagator is derived from thermodynamic force and entropy fluctuation operators that are in general non-linear.

Introduction

What is the probability operator for a non-equilibrium quantum system?

This paper develops the formal theory of non-equilibrium quantum statistical mechanics in terms analogous to the author's theory for the classical non-equilibrium case,¹⁻⁴ which was itself built on an earlier approach to classical equilibrium theory.^{5,6} The present work uses recent analysis of equilibrium quantum statistical mechanics,⁷⁻⁹ which in general this reproduces conventional text book results,¹⁰⁻¹² but with the theory formulated in terms of the wave function and wave space.⁷ The main new result of that work was the derivation of the stochastic, dissipative Schrödinger equation for an open equilibrium quantum system.⁸

In order to demonstrate clearly the gap in the current state of knowledge that the present paper fills, consider the simplest non-equilibrium system, namely one in which the energy operator on the sub-system is time-dependent, $\hat{H}(t)$, with the sub-system being open and able to exchange energy with a thermal reservoir of temperature T . For such a mechanical non-equilibrium system, the non-equilibrium probability operator is not simply the equilibrium Maxwell-Boltzmann probability operator evaluated at time t ,

$$\hat{\rho}(t) \neq \frac{1}{Z(t, T)} e^{-\hat{H}(t)/k_B T},$$

where k_B is Boltzmann's constant. Almost all books and papers that invoke a time-dependent potential assert or assume that this is the non-equilibrium probability operator. However, it is easy to show that this is not correct.

The second law of thermodynamics says that for a non-equilibrium system, the entropy must increase in the positive time direction. In consequence, the non-equilibrium probability operator must possess a time asymmetry that distinguishes between the future and the past. Since complex conjugation of an operator corresponds to velocity reversal, this means that the non-equilibrium probability operator must be complex, $\hat{\rho}(t)^* \neq \hat{\rho}(t)$. But since the Hamiltonian operator is real, $\hat{H}(t)^* = \hat{H}(t)$, this proves that the Maxwell-Boltzmann probability operator cannot be the probability operator for a non-equilibrium system.

The correct non-equilibrium probability operator is herein derived for generic mechanical and thermody-

namic non-equilibrium systems. The detailed physical justification and motivation for the various definitions that follow may be found in Ch. 8 of Ref. [3]. The present quantum derivation follows the recently simplified classical version.⁴

A second contribution of the present paper to non-equilibrium quantum statistical mechanics is the derivation of the stochastic, dissipative Schrödinger equation for open non-equilibrium systems. It turns out that this derivation involves non-linear quantum operators.

Research on non-linear operators in quantum mechanics may be grouped into three main themes: the formulation of non-linear quantum mechanics,¹³⁻¹⁹ the non-linear Schrödinger equation,²⁰⁻²⁹ and the non-linear Schrödinger equation including dissipation or friction.³⁰⁻³⁸ In many cases the type of non-linearity is simply postulated and the emphasis is on the consequences of the chosen form. In the present paper the non-linear thermodynamic force operator arises in the first principles derivation and there is no ambiguity about its final form or specific role in the dissipative Schrödinger equation. Although this aspect of the present work belongs to the third category just mentioned, detailed comparison will not be made here because non-linearity *per se* is not the primary focus of the present work, and also because in the final form the non-linearity reduces to a scale factor that only weakly influences the results.

I. RESERVOIR ENTROPY

A. Trajectory Entropy

The total system is isolated and is composed of a sub-system and a reservoir. The reservoir is also known as the environment, or the thermal bath, and the sub-system is also known as an open system. For the mechanical system with time-dependent external potential acting on the sub-system, $\hat{H}(t) = \hat{H}_0 + \hat{U}_{\text{ext}}(t)$, the total energy at time t is the sum of that of the sub-system and that of the reservoir $E_{\text{tot}}(t) = E_s(t) + E_r(t)$. Since the total system is isolated, the change in the total energy from some initial time is the work performed on the sub-system by the time-dependent external potential. An expression for this work will be given shortly.

When the sub-system is in the wave state ψ , its energy

is

$$E_s(\psi, t) = \frac{1}{N(\psi)} \langle \psi | \hat{\mathcal{H}}(t) | \psi \rangle. \quad (1.1)$$

Here and throughout the magnitude of the wave function is $N(\psi) = \langle \psi | \psi \rangle$.

In this paper the adiabatic rate of change is defined as the evolution of the sub-system considered as isolated. An adiabatic sub-system evolves according to the deterministic Schrödinger equation. In the present paper the adiabatic rate of change of a quantity is denoted by an over-dot and the superscript 0. Accordingly, the adiabatic rate of change of the sub-system energy is

$$\begin{aligned} \dot{E}_s^0(\psi, t) &= \frac{-\dot{N}^0(\psi)}{N(\psi)} E_s(\psi, t) + \frac{1}{N(\psi)} \langle \dot{\psi}^0 | \hat{\mathcal{H}}(t) | \psi \rangle \\ &\quad + \frac{1}{N(\psi)} \langle \psi | \hat{\mathcal{H}}(t) | \dot{\psi}^0 \rangle + \frac{1}{N(\psi)} \langle \psi | \partial_t \hat{\mathcal{H}}(t) | \psi \rangle \\ &= \frac{1}{N(\psi)} \langle \psi | \partial_t \hat{\mathcal{H}}(t) | \psi \rangle, \end{aligned} \quad (1.2)$$

where $\partial_t \equiv \partial/\partial t$. The constancy of the magnitude and of the energy along the adiabatic trajectory are well-known.^{8,10–12} Consequently all terms vanish except the expectation value of the partial time derivative of the energy operator. This single non-vanishing term represents the rate at which work is done on the sub-system by the external potential. Although the *rate* at which work is done on the sub-system does not depend upon the trajectory (i.e. whether it is adiabatic for a closed system, or whether it is dissipative and stochastic for an open system), the *total* work done depends upon the actual trajectory up to the present wave state.

In general, a trajectory in the open sub-system, which is not the adiabatic trajectory, must conserve the magnitude of the wave function, $N(\psi(t)) = N(\psi(0)) \equiv N_0$, or

$$\dot{N}(\psi(t)) = 0. \quad (1.3)$$

For the adiabatic evolution it can be shown directly that $\dot{N}^0(\psi(t)) = 0$. For an equilibrium open system, the constancy of the magnitude occurs because the time propagator is on average unitary as a consequence of the reduction condition on the transition probability operator (see §IIC of Ref. 9). It is also unitary in the non-equilibrium case (see §IV of Ref. 9 and Eq. (1.22) below).

At time t , denote by $\psi(t)$ the current wave state of the sub-system, and denote by $\psi[t]$ the trajectory of the sub-system, which is to say all of the wave states leading up to the current state. The total work done on the sub-system is a functional of the trajectory. Unlike the sub-system energy, for example, which depends solely on the present state of the system, the work done depends upon how the system got to the present state. It is given by

$$W(\psi[t]) = \int_0^t dt' \frac{1}{N(\psi(t'))} \langle \psi(t') | \partial_{t'} \hat{\mathcal{H}}(t') | \psi(t') \rangle$$

$$= \int_0^t dt' \dot{E}_s^0(\psi(t'), t'). \quad (1.4)$$

Although the focus at present is on mechanical non-equilibrium systems, the formalism is designed to apply as well to thermodynamic non-equilibrium systems. The final equality here is readily expressed in terms of the adiabatic rate of change of the so-called static part of the reservoir entropy, and as such it holds also for thermodynamic non-equilibrium systems, as is discussed following Eq. (1.36) below.

The total energy at all times is the sum of that of the sub-system and that of the reservoir $E_{\text{tot}}(t) = E_s(t) + E_r(t)$, irrespective of the total wave state or the history of the system. Because the total system is isolated, the rate of change of the total energy is equal to the rate at which work is being done on the sub-system, so that one also has $E_{\text{tot}}(\psi[t]) = E_{\text{tot}}(0) + W(\psi[t])$. Here the dependence on a particular trajectory of the sub-system is shown. With these, the reservoir energy for a given sub-system trajectory is

$$E_r(\psi[t]) = \text{const.} + W(\psi[t]) - E_s(\psi(t), t). \quad (1.5)$$

The constant is just the starting total energy. This can be neglected here and below since the start of a long enough trajectory is uncorrelated with the current position. Note that $\psi[t]$ is the trajectory of the wave function of the sub-system, so that this result gives the reservoir energy irrespective of the reservoir wave state or its history.

Contrast this result with the equilibrium case when the energy operator is not a function of time. In such a case $E_r(\psi) = \text{const.} - E_s(\psi)$. This only depends upon the current wave state of the sub-system, not upon its previous history.⁷

Using the standard thermodynamic result that the inverse temperature is the energy derivative of the entropy,⁶ $T^{-1} = \partial S(E)/\partial E$, and the fact that the reservoir is infinitely larger than the sub-system, a Taylor expansion shows that the reservoir entropy for a particular trajectory of the sub-system is

$$\begin{aligned} S_r^{<>}(\psi[t]) &= \text{const.} + \frac{E_r(\psi[t])}{T} \\ &= \text{const.} + \frac{W(\psi[t]) - E_s(\psi(t), t)}{T}. \end{aligned} \quad (1.6)$$

Again this can be contrasted with the equilibrium result of $S_r^{<>}(\psi) = \text{const.} - E_s(\psi)/T$. In the language of Ref. [8], this is the expectation trajectory entropy rather than the actual trajectory entropy, as is discussed below.

In paper I,⁷ it was shown that wave states of an isolated system are uniformly weighted. In consequence, the weight of sub-system wave states is proportional to the total weight of the reservoir states for a given sub-system wave state, which itself is proportional to the exponential of the reservoir entropy in the given sub-system wave state. Hence the reservoir entropy is the same as the total entropy $S_{\text{tot}}(\psi[t]) = S_r(\psi[t])$, and similarly for the

operators. In this paper the notation S_r rather than S_{tot} will be used, and it will as often be called ‘the entropy’ as ‘the reservoir entropy’. In paper III⁹ it was established in a generic fashion that the exponential of the entropy operator is the probability operator. In the present non-equilibrium case one expects instead to be dealing with operator functionals, at least initially.

Define the expectation functional $O(\psi[t])$ as an operator that has expectation value over a trajectory of

$$\begin{aligned} O(\psi[t]) &\equiv \frac{\langle \psi[t] | \hat{O}[t] | \psi[t] \rangle}{\langle \psi[t] | \psi[t] \rangle} \\ &\equiv \int_0^t dt' \frac{\langle \psi(t') | \hat{O}(t') | \psi(t') \rangle}{\langle \psi(t') | \psi(t') \rangle} \\ &= \frac{1}{N_0} \int_0^t dt' \langle \psi(t') | \hat{O}(t') | \psi(t') \rangle, \quad (1.7) \end{aligned}$$

since $N(\psi(t')) \equiv N_0$. The work done over a trajectory is of this form.

The sub-system energy that appears in Eq. (1.5) *et seq.*, instead of being written in terms of the current wave state, as in Eq. (1.1), can be written as an integral of the total differential over the trajectory,

$$E_s(\psi(t), t) = E_s(\psi(0), 0) + \int_0^t dt' \frac{dE_s(\psi(t'), t')}{dt'}. \quad (1.8)$$

With this and the expression for the work done, Eq. (1.4), the expectation entropy for the trajectory, Eq. (1.6), can be written

$$\begin{aligned} S_r^{<>}(\psi[t]) &= \text{const.}' - \frac{1}{T} \int_0^t dt' \left\{ \frac{dE_s(\psi(t'), t')}{dt'} - \dot{E}_s^0(\psi(t'), t') \right\} \\ &= \text{const.}' - \frac{1}{T} \int_0^t dt' \left\{ \frac{-\dot{N}(\psi(t'))}{N(\psi(t'))} E_s(\psi(t'), t') \right. \\ &\quad \left. + \frac{1}{N(\psi(t'))} \langle \dot{\psi}(t') | \hat{\mathcal{H}}(t') | \psi(t') \rangle \right. \\ &\quad \left. + \frac{1}{N(\psi(t'))} \langle \psi(t') | \hat{\mathcal{H}}(t') | \dot{\psi}(t') \rangle \right\} \\ &= \text{const.}' - \frac{1}{TN_0} \int_0^t dt' \left\{ \langle \dot{\psi}(t') | \hat{\mathcal{H}}(t') | \psi(t') \rangle \right. \\ &\quad \left. + \langle \psi(t') | \hat{\mathcal{H}}(t') | \dot{\psi}(t') \rangle \right\} \\ &= \text{const.}' - \frac{1}{TN_0} \int_0^t dt' \left\{ \langle \psi(t') | \hat{d}_t^\dagger \hat{\mathcal{H}}(t') | \psi(t') \rangle \right. \\ &\quad \left. + \langle \psi(t') | \hat{\mathcal{H}}(t') \hat{d}_t | \psi(t') \rangle \right\}. \quad (1.9) \end{aligned}$$

The third equality invokes the constancy of the magnitude. In this form it is clear that only the non-adiabatic terms contribute, since $\hat{d}_t \psi(t) \equiv d\psi(t)/dt \equiv \dot{\psi}(t)$ can be replaced by $\dot{\psi}(t) - \dot{\psi}^0(t)$ in the penultimate equality without changing the result.

The physical interpretation and justification of this result is straightforward. The change in reservoir entropy is

due to the change in reservoir energy, which is equal and opposite to the reservoir-induced change in sub-system energy. The reservoir-induced change in sub-system energy is equal to the total change in sub-system energy, less the adiabatic change in sub-system energy. The latter is just the work done on the sub-system by the time varying external potential. One sees therefore that the integrand of the first equality above is the total rate of change less the adiabatic rate of change of the sub-system energy, as required.

From the final equality one sees that the reservoir entropy trajectory operator at time t' is

$$\hat{S}_r[t'] \equiv \frac{-1}{T} \left\{ \hat{d}_t^\dagger \hat{\mathcal{H}}(t') + \hat{\mathcal{H}}(t') \hat{d}_t \right\}, \quad t' \leq t. \quad (1.10)$$

Even though this is a local function of time it only has meaning in the context of a time integral over the trajectory. In order to make this clear, brackets are used to encase the argument on the left hand side. This distinguishes it from the reservoir entropy operator $\hat{S}_r(t)$ that is given shortly and that is to be used in conjunction with an ordinary expectation value at time t . The conjugate time derivative $\hat{d}_t^\dagger \equiv (d/dt)^\dagger$ acts to the left. This reservoir entropy operator is clearly Hermitian. This result will shortly become the analogue of Eq. (8.16) of Ref. [3].

What is ultimately required is $\hat{\phi}(t)$, the probability operator at time t for the non-equilibrium system. How this is derived from the above reservoir entropy operator functional (equivalently, entropy trajectory operator) is the subject of §IC. Prior to that, certain properties of the transition probability operator and time propagator are established for later use.

B. Transition Probability Operator and Propagator

Let $\hat{\phi}(t)$ be the non-equilibrium probability operator at time t , which will be given explicitly below, and let $\hat{\phi}^{(2)}(t_2, t_1)$ be the unconditional transition probability operator for the transition $\{\psi_1, t_1\} \rightarrow \{\psi_2, t_2\}$. The latter obeys the reduction condition⁹

$$\text{Tr}_1^{(1)} \hat{\phi}^{(2)}(t_2, t_1) = \hat{\phi}(t_2), \quad (1.11)$$

and, analogously, $\text{Tr}_2^{(1)} \hat{\phi}^{(2)}(t_2, t_1) = \hat{\phi}(t_1)$. The subscript on the trace indicates which time is summed over. The superscript on the one time probability operator is dropped for simplicity, $\hat{\phi}(t) \equiv \hat{\phi}^{(1)}(t)$.

One can define a stochastic dissipative time propagator that gives the evolution of the wave function in the open non-equilibrium system,

$$|\psi(t_2)\rangle = \hat{U}(t_2, t_1) |\psi(t_1)\rangle. \quad (1.12)$$

An explicit expression for the propagator will be obtained below. If $t_2 < t_1$, this is a backward trajectory, and if $t_2 > t_1$, it is a forward trajectory.

The conditional transition probability operator is a two-time operator that can be written as the composition of the two one-time time propagators,⁹

$$\hat{\rho}^{(2),\text{cond}}(t_2, t_1) = \left\langle \left\{ \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \right\} \right\rangle_{\text{stoch}}. \quad (1.13)$$

The notation $\langle \dots \rangle_{\text{stoch}}$ signifies the average over the stochastic operators in the propagator. Accordingly the unconditional transition probability operator is the composition of the conditional transition probability operator and the singlet probability operator that can be arranged in four ways,

$$\begin{aligned} \hat{\rho}^{(2)}(t_2, t_1) &= \left\langle \left\{ \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \hat{\rho}(t_1) \right\} \right\rangle_{\text{stoch}} \\ &= \left\langle \left\{ \hat{\rho}(t_1) \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \right\} \right\rangle_{\text{stoch}} \\ &= \left\langle \left\{ \hat{U}(t_2, t_1)^\dagger, \hat{\rho}(t_2) \hat{U}(t_2, t_1) \right\} \right\rangle_{\text{stoch}} \\ &= \left\langle \left\{ \hat{U}(t_2, t_1)^\dagger \hat{\rho}(t_2), \hat{U}(t_2, t_1) \right\} \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.14)$$

Taking the traces of this and using the reduction condition, one obtains the stationarity condition and the unitary condition for the propagator. Taking the trace over t_1 one obtains

$$\begin{aligned} \hat{\rho}(t_2) &= \left\langle \hat{U}(t_2, t_1) \hat{\rho}(t_1) \hat{U}(t_2, t_1)^\dagger \right\rangle_{\text{stoch}} \\ &= \hat{\rho}(t_2) \left\langle \hat{U}(t_2, t_1) \hat{U}(t_2, t_1)^\dagger \right\rangle_{\text{stoch}}, \end{aligned} \quad (1.15)$$

and taking the trace over t_2 one obtains

$$\begin{aligned} \hat{\rho}(t_1) &= \left\langle \hat{U}(t_2, t_1)^\dagger \hat{U}(t_2, t_1) \right\rangle_{\text{stoch}} \hat{\rho}(t_1) \\ &= \left\langle \hat{U}(t_2, t_1)^\dagger \hat{\rho}(t_2) \hat{U}(t_2, t_1) \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.16)$$

The two equations not shown in each case are identical to those shown. Ordinary composition of one-time operators is indicated by the juxtaposition of operators in these equations and in those that follow. The second equality of the first set, and the first equality of the second set, imply the unitary condition,

$$\begin{aligned} \hat{I} &= \left\langle \hat{U}(t_2, t_1)^\dagger \hat{U}(t_2, t_1) \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{U}(t_2, t_1) \hat{U}(t_2, t_1)^\dagger \right\rangle_{\text{stoch}}, \end{aligned} \quad (1.17)$$

and this has complex conjugate

$$\begin{aligned} \hat{I} &= \left\langle \hat{U}(t_2, t_1)^T \hat{U}(t_2, t_1)^* \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{U}(t_2, t_1)^* \hat{U}(t_2, t_1)^T \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.18)$$

The first equality of the first set of equations, and the second equality of the second set of equations, imply the stationarity condition,

$$\begin{aligned} \hat{\rho}(t_2) &= \left\langle \hat{U}(t_2, t_1) \hat{\rho}(t_1) \hat{U}(t_2, t_1)^\dagger \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{U}(t_1, t_2)^\dagger \hat{\rho}(t_1) \hat{U}(t_1, t_2) \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.19)$$

The nomenclature ‘stationarity’ derives from the equilibrium case. In the present non-equilibrium situation it might be better to call it the stability condition, by which is meant that the form derived for the probability operator as a function of time has to be consistent with the time evolution of the probability operator given by this equation.

Now

$$\hat{\rho}(t)^\dagger = \hat{\rho}(t) \text{ but } \hat{\rho}(t)^* \neq \hat{\rho}(t). \quad (1.20)$$

The right hand side of the stationarity condition is obviously Hermitian. The complex conjugate of the stationarity condition is

$$\begin{aligned} \hat{\rho}(t_2)^* &= \left\langle \hat{U}(t_2, t_1)^* \hat{\rho}(t_1)^* \hat{U}(t_2, t_1)^T \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{U}(t_1, t_2)^T \hat{\rho}(t_1)^* \hat{U}(t_1, t_2)^* \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.21)$$

The unitary nature of the time propagator implies that on average the magnitude of the wave function is constant on a trajectory. That is,

$$\begin{aligned} \langle N(\psi(t'|\psi_0, t_0)) \rangle_{\text{stoch}} &= \left\langle \langle \psi(t'|\psi_0, t_0) | \psi(t'|\psi_0, t_0) \rangle \right\rangle_{\text{stoch}} \\ &= \left\langle \langle \psi_0 | \hat{U}(t', t)^\dagger \hat{U}(t', t) | \psi_0 \rangle \right\rangle_{\text{stoch}} \\ &= N(\psi_0). \end{aligned} \quad (1.22)$$

Here and often below the wave function trajectory starting at $\{\psi_0, t_0\}$ is written $\psi(t'|\psi_0, t_0)$ rather than the simpler $\psi(t')$ used above.

1. Operator Evolution

The time development of an operator can be derived from the expectation value

$$\begin{aligned} O(\psi(t|\psi_0, t_0), t) &= \frac{1}{N_0} \langle \psi(t|\psi_0, t_0) | \hat{O}(t) | \psi(t|\psi_0, t_0) \rangle \\ &= \frac{1}{N_0} \langle \psi_0 | \hat{U}(t, t_0)^\dagger \hat{O}(t) \hat{U}(t, t_0) | \psi_0 \rangle. \end{aligned} \quad (1.23)$$

Hence

$$\hat{O}(t, t_0) = \left\langle \hat{U}(t, t_0)^\dagger \hat{O}(t) \hat{U}(t, t_0) \right\rangle_{\text{stoch}} \quad (1.24)$$

is the evolved operator to be used in conjunction with the original wave state at time t_0 . The stochastic average of this has been taken. Note the similarities and differences between this expression for the observable operator evolution and that for the probability operator evolution, Eq. (1.19).

The time derivative of the evolved operator (with respect to the final state) is

$$\begin{aligned} \left. \frac{d\hat{O}(t, t_0)}{dt} \right|_{t_0 \rightarrow t} &\equiv \hat{\dot{O}}(t) \\ &= \partial_t \hat{O}(t) + \hat{\tilde{U}}(t)^\dagger \hat{O}(t) + \hat{O}(t) \hat{\tilde{U}}(t) \\ &\quad + \frac{1}{\tau} \left\langle \hat{\tilde{R}}(\tau, t)^\dagger \hat{O}(t) \hat{\tilde{R}}(\tau, t) \right\rangle_{\text{stoch}}, \end{aligned} \quad (1.25)$$

with $\tau \equiv t - t_0 \rightarrow 0$. This is the total (or convective, or hydrodynamic) time derivative. It takes into account the changes in the expectation value of the operator as the system moves along its trajectory in wave space. It expresses the propagator as the sum of a most likely part and a stochastic part of zero mean, $\hat{U} = \hat{\tilde{U}} + \hat{\tilde{R}}$, as will be given explicitly later. Due to irreversibility, $\hat{\tilde{U}}(t)$ depends upon the sign of τ , and one should be careful to specify whether the forward or backward derivative is required. The partial time derivative, which only accounts for the changes in the operator due to its explicit time dependence, is denoted $\partial_t \hat{O}(t) \equiv \partial \hat{O}(t) / \partial t$. The adiabatic total time derivative of an operator is

$$\begin{aligned} \hat{\dot{O}}^0(t) &\equiv \partial_t \hat{O}(t) + \hat{U}^0(t)^\dagger \hat{O}(t) + \hat{O}(t) \hat{U}^0(t) \\ &= \partial_t \hat{O}(t) - \frac{1}{i\hbar} \hat{H}(t) \hat{O}(t) + \frac{1}{i\hbar} \hat{O}(t) \hat{H}(t) \end{aligned} \quad (1.26)$$

C. Point Entropy

1. Average Propagator Product

The approach taken in §8.2.2 of Ref. [3] for obtaining the non-equilibrium probability density of a classical phase space point from the non-equilibrium classical trajectory probability is now converted into quantum terms. The analogous quantum procedure would be to go from a trajectory to a wave state (or from an expectation value functional to an expectation value) by replacing the arbitrary trajectory $\psi[t]$ by the most likely trajectory that passes through the wave state ψ at time t , which may be denoted $\bar{\psi}(t|\psi, t)$. However, in the quantum case it turns out that the stochastic average over the trajectories rather than the most likely trajectory is required.

To see why, the most likely trajectory can be expressed in terms of the most likely time propagator,

$$|\bar{\psi}(t'|\psi, t)\rangle = \hat{\tilde{U}}(t', t)|\psi\rangle. \quad (1.27)$$

The most likely propagator and the average propagator are equal,

$$\left\langle \hat{U}(t', t) \right\rangle_{\text{stoch}} = \hat{\tilde{U}}(t', t). \quad (1.28)$$

However, due to correlations, the average of the product is not equal to the product of the averages,

$$\left\langle \hat{U}(t', t)^\dagger \hat{U}(t', t) \right\rangle_{\text{stoch}} \neq \hat{\tilde{U}}(t', t)^\dagger \hat{\tilde{U}}(t', t). \quad (1.29)$$

(From the above, the left hand side is the unit operator.) In what follows, the product of the propagators appears, and it is for this reason the point reservoir entropy is formulated as the stochastic average of the reservoir trajectory entropy.

2. Reduction of the Trajectory Entropy

The trajectory may be written in terms of the propagator as $|\psi(t')\rangle \equiv |\psi(t')|\psi, t\rangle \equiv \hat{U}(t', t)|\psi\rangle$. The reservoir entropy operator that was to be used in conjunction with a time integral over the trajectory was given above as Eq. (1.10)

$$\hat{S}_r[t'] \equiv \frac{-1}{T} \left\{ \hat{d}_t^\dagger \hat{H}(t') + \hat{H}(t') \hat{d}_t \right\}, \quad t' \leq t. \quad (1.30)$$

This acts on the trajectory itself, $|\psi[t']|\psi, t\rangle$. In view of the propagator form for the trajectory, one may alternatively define the reservoir entropy operator for the trajectory as

$$\begin{aligned} \hat{S}_r[t'; t] &\equiv \hat{U}(t', t)^\dagger \hat{S}_r[t'] \hat{U}(t', t) \\ &= \frac{-1}{T} \hat{U}(t', t)^\dagger \left\{ \hat{d}_t^\dagger \hat{H}(t') + \hat{H}(t') \hat{d}_t \right\} \hat{U}(t', t). \end{aligned} \quad (1.31)$$

This acts on the current wave function $|\psi\rangle$.

The expectation entropy for the trajectory, Eq. (1.9), can be equally well written in terms of either of these,

$$\begin{aligned} S_r^{<>}(\psi[t]) &= \frac{1}{N_0} \int_0^t dt' \langle \psi(t') | \hat{S}_r[t'] | \psi(t') \rangle \\ &= \frac{1}{N_0} \int_0^t dt' \langle \psi | \hat{S}_r[t'; t] | \psi \rangle, \end{aligned} \quad (1.32)$$

where the magnitude $N_0 \equiv \langle \psi(t') | \psi(t') \rangle$ is constant on the trajectory.

One may average over the stochastic trajectories and perform the time integral to obtain the reservoir entropy operator for a wave state at time t ,

$$\hat{S}_r(t) \equiv \int_0^t dt' \left\langle \hat{S}_r[t'; t] \right\rangle_{\text{stoch}}. \quad (1.33)$$

This is a single time operator that is evaluated in explicit detail below. In terms of this the expectation entropy for the current wave state ψ is

$$S_r^{<>}(\psi, t) = \frac{\langle \psi | \hat{S}_r(t) | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (1.34)$$

and the actual entropy is

$$S_r(\psi, t) = k_B \ln \frac{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (1.35)$$

For the distinction between the expectation entropy and the actual entropy, see Eqs (1.30) and (1.31) of Ref. [9]; it

is the actual entropy that fundamentally gives the probability density of the wave state.

Taking the time integral of the stochastic average of reservoir entropy trajectory operator $\hat{S}_r[t'; t]$ reduces it to the single time operator $\hat{S}_r(t)$. The latter is *the* reservoir entropy operator for the non-equilibrium system. As such the expression (1.33) is a manifestation of the reduction condition.

The reduction condition^{3,39} in its original form stated that the second entropy of two states evaluated at the optimum value of one of the states is equal to the first entropy of the other state. The reduction condition is essentially a statement that fluctuations contribute negligibly to the entropy, in which case the optimum value is the same as the average value. Originally derived for classical systems, the quantum analogue has also been shown to hold.⁹ An important outcome of the quantum analysis was the distinction between the expectation entropy and the actual entropy, and the conclusion that it was the actual entropy to which the reduction condition applied.⁹

Because of the close relationship between entropy and probability, the reduction condition on the entropy is similar to, but not precisely the same as, the reduction condition on the transition probability, Eq. (1.11). The latter involves a sum over all states, whereas the former takes the logarithm of that sum and singles out the most likely state as dominant.

The reduction condition can obviously be generalized to larger sets of states.³ In the case of a trajectory, it says that if the trajectory is optimized with respect to all points except the final one, then the trajectory entropy is equal to the ordinary (first) entropy of that terminal point. Equivalently, the stochastic average over all points on the trajectory except one reduces the trajectory entropy to the state entropy of the remaining point.

Strictly speaking, there should be added to the expression for the reservoir entropy, Eq. (1.33), a constant operator in wave space, namely the identity operator multiplied by a time-dependent scalar that is the difference between the current time value of the reservoir entropy and the running time average of the reservoir entropy,

$$\left[\overline{S}_r(t) - \frac{1}{t} \int_0^t dt' \overline{S}_r(t') \right] \hat{1}.$$

This is the analogue of the scale factors for the reduction condition on the non-equilibrium weights (see Eq. (4.4) of Ref. [9], and Eq. (8.38) of Ref. [3]). Although this constant has a definite physical interpretation, it can be discarded (i.e. incorporated into the normalizing partition function for the probability operator) without affecting any statistical average. As such, $S_r(\psi, t)$ is more precisely called the wave state dependent part of the reservoir entropy at the current time.

3. Form and Interpretation of the Point Entropy

The reservoir (equivalently total) entropy operator, Eq. (1.33), in the case of a mechanical non-equilibrium system may be explicitly written and rearranged as

$$\begin{aligned} \hat{S}_r(t) &= \frac{-1}{T} \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger \hat{d}_t^\dagger \hat{H}(t') \hat{U}(t', t) \right. \\ &\quad \left. + \hat{U}(t', t)^\dagger \hat{H}(t') \hat{d}_t \hat{U}(t', t) \right\rangle_{\text{stoch}} \\ &= \frac{-1}{T} \hat{H}(t) + \frac{1}{T} \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger (\partial_{t'} \hat{H}(t')) \hat{U}(t', t) \right\rangle_{\text{stoch}} \\ &\equiv \hat{S}_{\text{st}}(t) - \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger \hat{S}_{\text{st}}^0(t') \hat{U}(t', t) \right\rangle_{\text{stoch}} \\ &\equiv \hat{S}_{\text{st}}(t) + \hat{S}_{\text{dyn}}(t). \end{aligned} \quad (1.36)$$

The steps in this derivation will be justified and interpreted below, but first it is noted that in the final equality the non-equilibrium reservoir entropy operator has been split into so-called static and dynamic parts. This result holds in general not just for the mechanical non-equilibrium case in which it was derived.

The static part is essentially the equilibrium expression that one would write down for the system. It gives predominantly the structure, and it is insensitive to the direction of time (i.e. the direction of the molecular velocities), $\hat{S}_{\text{st}}(t)^* = \hat{S}_{\text{st}}(t)$. For the non-equilibrium mechanical system it is just the Maxwell-Boltzmann form, $\hat{S}_{\text{st}}(t) = -\hat{H}(t)/T$.

The dynamic part part of the non-equilibrium reservoir entropy is sensitive to the direction of time, $\hat{S}_{\text{dyn}}(t)^* \neq \hat{S}_{\text{dyn}}(t)$. Explicitly it is

$$\hat{S}_{\text{dyn}}(t) = - \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger \hat{S}_{\text{st}}^0(t') \hat{U}(t', t) \right\rangle_{\text{stoch}}. \quad (1.37)$$

In essence this subtracts the total adiabatic change in the static part of the reservoir entropy up to the present time. The adiabatic derivative of the static part of the reservoir entropy is

$$\hat{S}_{\text{st}}^0(t) = \partial_t \hat{S}_{\text{st}}(t) - \frac{1}{i\hbar} \hat{H}(t) \hat{S}_{\text{st}}(t) + \frac{1}{i\hbar} \hat{S}_{\text{st}}(t) \hat{H}(t). \quad (1.38)$$

For the non-equilibrium mechanical system this is just $\hat{S}_{\text{st}}^0(t) = -\partial_t \hat{H}(t)/T$.

Returning to the discussion of Eq. (1.36), the passage from the first equality to the second equality follows an integration by parts and the fact that $\hat{U}(t, t) = \hat{1}$. Due to the conservation of energy on an adiabatic trajectory, the partial time derivative of the energy operator is equal to its adiabatic time derivative, $\partial_t \hat{H}(t) = \hat{H}^0(t)$. One can see therefore in the penultimate equality that the integrand is the adiabatic rate of change of the sub-system energy at time t' , and so the difference between the first term on the left hand side of the penultimate equality and

the integral is the change in energy of the sub-system induced by the reservoir, all divided by temperature. This is in accord with the physical interpretation offered following Eq. (1.9) above.

In the penultimate equality of Eq. (1.36) has been defined the static part of the reservoir entropy operator for a mechanical non-equilibrium system,

$$\hat{S}_{\text{st}}(t) = \frac{-1}{T} \hat{\mathcal{H}}(t). \quad (1.39)$$

This of course is just the instantaneous reservoir entropy operator for a thermal equilibrium system. The reason for casting the reservoir entropy operator for a non-equilibrium system in the above terms of the equilibrium entropy operator is that the formalism carries through with only minor changes for a thermodynamic non-equilibrium system. A thermodynamic non-equilibrium system consists of a sub-system sandwiched between two reservoirs that apply a thermodynamic gradient. This is the configuration that typically gives steady state flows; heat flow, electric current, hydrodynamic flow, and diffusive flux are common examples. Explicitly, for steady heat flow

$$\hat{S}_{\text{st}}(t) = \frac{-\hat{E}_0}{T_0} - \frac{\hat{E}_1}{T_1}. \quad (1.40)$$

where T_0 is essentially the average temperature of the two reservoirs and T_1 is essentially the temperature gradient between the two reservoirs, and where $\hat{E}_0 \equiv \hat{\mathcal{H}}$ and \hat{E}_1 are the zeroth and first energy moment operators, respectively. Whereas for a mechanical system with time-independent Hamiltonian the adiabatic evolution of the energy operator vanishes, for steady heat flow the adiabatic evolution of the first energy moment is non-zero. See Refs [3,40,41] for full details in the classical case.

The physical interpretation of the third equality of Eq. (1.36) is essentially the same as the interpretation of the second equality, but it is a little more general because it encompasses both mechanical and thermodynamic non-equilibrium systems. The static reservoir entropy is expressed solely in terms of sub-system properties, so it in itself is not the actual reservoir entropy. However, subtracting the total adiabatic change of the static reservoir entropy from the current value of the static reservoir entropy gives the change (from its value at $t = 0$) in the static reservoir entropy that is due solely to the interactions with the reservoir. It is this quantity that is the actual (change in the) reservoir entropy.

Of the two contributions to the reservoir entropy of the non-equilibrium system, the static part dominates for the structure, but the dynamic term is essential to get the irreversible aspects of a non-equilibrium system correct. This dynamic term is the non-trivial part of the entropy for a non-equilibrium system. The Green-Kubo relations,⁴²⁻⁴⁴ which express the transport coefficients as an integral of certain equilibrium time correlation functions, come directly from this dynamic part.^{1,3,4}

4. Non-Equilibrium Probability Operator

Using the non-equilibrium reservoir entropy operator, Eq. (1.36), the probability operator for a mechanical or thermodynamic non-equilibrium quantum system is

$$\begin{aligned} \hat{\phi}(t) &= \frac{1}{Z(t)} e^{\hat{S}_{\text{r}}(t)/k_{\text{B}}} \\ &= \frac{1}{Z(t)} e^{\{\hat{S}_{\text{st}}(t) + \hat{S}_{\text{dyn}}(t)\}/k_{\text{B}}} \\ &= \frac{1}{Z(t)} \exp \frac{1}{k_{\text{B}}} \left\{ \hat{S}_{\text{st}}(t) \right. \\ &\quad \left. - \int_0^t dt' \left\langle \hat{\mathcal{U}}(t', t)^\dagger \hat{S}_{\text{st}}^0(t') \hat{\mathcal{U}}(t', t) \right\rangle_{\text{stoch}} \right\}. \end{aligned} \quad (1.41)$$

Here $Z(t)$ is just the normalizing partition function. This relies upon the result derived in paper I:⁷ due to wave function collapse, the probability operator is the exponential of the entropy operator divided by Boltzmann's constant. (That result was derived for a canonical equilibrium system.) One persuasive reason to believe that the present result is the correct expression for the non-equilibrium probability operator is that keeping only the leading order term reduces the present expression to the equilibrium probability operator, $\hat{\phi}_{\text{equil}} = e^{\hat{S}_{\text{st}}/k_{\text{B}}}/Z$.

The non-equilibrium statistical average of a one-time operator is

$$\begin{aligned} \langle \hat{O}(t) \rangle_{T,t} &= \int d\psi \frac{\langle \psi | \hat{\phi}(t) \hat{O}(t) | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \text{Tr}^{(1)} \hat{\phi}(t) \hat{O}(t). \end{aligned} \quad (1.42)$$

In view of the time evolution of the operator given above, Eq. (1.24), this can also be written

$$\begin{aligned} \langle \hat{O}(t_2) \rangle_{T,t} &= \text{Tr}^{(1)} \hat{\phi}(t_1) \hat{O}(t_2, t_1) \\ &= \text{Tr}^{(1)} \left\langle \hat{\phi}(t_1) \hat{\mathcal{U}}(t_2, t_1)^\dagger \hat{O}(t_2) \hat{\mathcal{U}}(t_2, t_1) \right\rangle_{\text{stoch}} \\ &= \text{Tr}^{(1)} \left\langle \hat{\mathcal{U}}(t_2, t_1) \hat{\phi}(t_1) \hat{\mathcal{U}}(t_2, t_1)^\dagger \hat{O}(t_2) \right\rangle_{\text{stoch}}. \end{aligned} \quad (1.43)$$

The final equality follows from the cyclic properties of the trace. Comparing this with Eq. (1.42) evaluated at t_2 , one sees that one must have

$$\hat{\phi}(t_2) = \left\langle \hat{\mathcal{U}}(t_2, t_1) \hat{\phi}(t_1) \hat{\mathcal{U}}(t_2, t_1)^\dagger \right\rangle_{\text{stoch}}. \quad (1.44)$$

This is the time evolution of the probability operator, and is in agreement with Eq. (1.19).

The expression for the non-equilibrium probability operator and for the non-equilibrium reservoir entropy operator are formally exact. However, to be useful, an explicit expression for the time propagator is required. This is the subject of §II. First, however, a fluctuation formulation of the non-equilibrium reservoir entropy is developed.

D. Fluctuation Form for the Reservoir Entropy

1. Ground State Projection

Label complete sets of microstates by either a single Roman letter such as n , or else by a Greek and Roman pair of letters, such as αh , where α is the principle quantum number, and h labels the degeneracy. A single Greek letter signifies a macrostate, which is a quantum state of an incomplete operator.

Let $\zeta_{\alpha h}^S(t)$ be an eigenfunction of the reservoir entropy, such that $\hat{S}_r(t)|\zeta_{\alpha h}^S(t)\rangle = S_\alpha(t)|\zeta_{\alpha h}^S(t)\rangle$, with $\alpha = 0, 1, 2, \dots$. The eigenstates of maximum entropy correspond to $\alpha = 0$, so that $S_\alpha(t) < S_0(t)$ for $\alpha > 0$. The sub-space corresponding to $\alpha = 0$ contains the most likely wave states, and it can also be called the entropy ground state. The projection operator for this is

$$\hat{P}_0(t) \equiv \sum_h |\zeta_{0h}^S(t)\rangle \langle \zeta_{0h}^S(t)|. \quad (1.45)$$

The projector for the orthogonal sub-space, the excited sub-space, is $\hat{P}_\perp(t) \equiv \hat{I} - \hat{P}_0(t)$.

In general an operator can be decomposed into its projections onto the two sub-spaces,

$$\begin{aligned} \hat{O} &= [\hat{P}_0 + \hat{P}_\perp] \hat{O} [\hat{P}_0 + \hat{P}_\perp] \\ &= \hat{P}_0 \hat{O} \hat{P}_0 + \hat{P}_0 \hat{O} \hat{P}_\perp + \hat{P}_\perp \hat{O} \hat{P}_0 + \hat{P}_\perp \hat{O} \hat{P}_\perp \\ &\equiv \hat{O}_{00} + \hat{O}_{0\perp} + \hat{O}_{\perp 0} + \hat{O}_{\perp\perp}. \end{aligned} \quad (1.46)$$

These are of course time dependent. The entropy operator is block diagonal,

$$\begin{aligned} \hat{S}_r(t) &= \hat{S}_{r,00}(t) + \hat{S}_{r,\perp\perp}(t) \\ &= S_0(t) \hat{P}_0(t) + \hat{S}_{r,\perp\perp}(t). \end{aligned} \quad (1.47)$$

2. Most Likely Trajectory

Now is introduced what will be called the most likely trajectory, $\bar{\psi}(t)$, although the nomenclature is not entirely satisfactory. One of two things will be meant by this: either this will be the ground state projection of the current wave state, $|\bar{\psi}(t)\rangle = \hat{P}_0(t)|\psi\rangle$, or else over a short time interval it is the most likely evolution of the ground state projection of the starting wave state, $|\bar{\psi}(t_2)\rangle = \hat{U}(t_2, t_1) \hat{P}_0(t_1)|\psi_1\rangle$. Hence one has

$$\hat{S}_r(t)|\bar{\psi}(t)\rangle = S_0(t)|\bar{\psi}(t)\rangle. \quad (1.48)$$

In the first case this is exact, and in the second case it is a good approximation for a short time interval.

The current wave state ψ can be considered in terms of the departure from the current value of the most likely trajectory. Hence the fluctuation at time t can be defined as

$$|\phi\rangle \equiv |\psi - \bar{\psi}(t)\rangle. \quad (1.49)$$

This is dominated by the excited states of the current wave state, $|\phi\rangle \approx \hat{P}_\perp(t)|\psi\rangle$ if $|\bar{\psi}(t)\rangle \approx \hat{P}_0(t)|\psi\rangle$. This would be exact if the current value of the most likely trajectory was taken as the ground state projection of the wave state. In general one expects the departure from the ground state to be small, and so this definition of a fluctuation provides the basis for an expansion of the entropy and other statistical mechanical properties.

The reason for being flexible with the definition the most likely trajectory is that the formalism is most useful in two different cases. The first case is for one-time thermodynamic properties such as the entropy, and this involves an expansion about the ground state projection of the current wave function. The second case is for two-time thermodynamic properties such as the second entropy, the transition probability, and the time propagator. These involve two fluctuation expansions: one about the ground state projection of the first wave function and the other about the most likely trajectory at the second time emanating from the first ground state projection. It turns out that the ground state projection of the most likely evolution is not equal to the most likely evolution of the ground state projection.

3. Fluctuation Operator and the Thermodynamic Force

Now the second derivative of the entropy will be given in order to write it in fluctuation form. First however a specifically quantum issue that does not arise in classical statistical mechanics must be addressed. As shown in Ref. [9], one must distinguish between the entropy and the expectation value of the entropy operator. This effects the form of the fluctuation matrix and the thermodynamic force.

As mentioned briefly in §IC, one has to distinguish between the actual entropy and the expectation entropy. The actual entropy, or simply entropy, is

$$S_r(\psi, t) \equiv k_B \ln \frac{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (1.50)$$

The expectation value of the entropy operator (expectation entropy, for short) is

$$S_r^{<>}(\psi, t) = \frac{\langle \psi | \hat{S}_r(t) | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (1.51)$$

If the sub-system is in an entropy macrostate, $|\psi_\alpha^S\rangle = \sum_h \psi_h |\zeta_{\alpha h}^S(t)\rangle$, these are equal,

$$S_r^{<>}(\psi_\alpha^S, t) = S_r(\psi_\alpha^S, t) = S_\alpha(t), \quad (1.52)$$

since $\hat{S}_r(t)|\psi_\alpha^S\rangle = S_\alpha(t)|\psi_\alpha^S\rangle$. They are also equal when linearization is valid, such as at high temperatures.

Below, wave state transitions will be analyzed via the second entropy with the object of deriving the stochastic, dissipative equation of motion for the non-equilibrium

system. The thermodynamic driving force will arise from the reduction condition on the second entropy in fluctuation form. As shown in Ref. [9], the reduction condition applies to the entropy, not to the expectation entropy. (Regrettably, the fluctuation and force operators derived in Ref. [9] are based on the expectation entropy, which is a linearization of the results subsequently given in Ref. [8] and that are given here.)

In view of this, the thermodynamic force is

$$\frac{\partial S_r(\psi, t)}{\partial \langle \psi |} = k_B \left[\frac{e^{\hat{S}_r(t)/k_B}}{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle} - \frac{1}{\langle \psi | \psi \rangle} \right] | \psi \rangle. \quad (1.53)$$

Hence the entropy force operator is defined as

$$\begin{aligned} \hat{S}'_r(\psi, t) &\equiv k_B \left[\frac{e^{\hat{S}_r(t)/k_B}}{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle} - \frac{1}{\langle \psi | \psi \rangle} \hat{\mathbf{I}} \right] \\ &= \frac{k_B}{N(\psi)} \left[\frac{e^{\hat{S}_r(t)/k_B}}{e^{S_r(\psi, t)/k_B}} - \hat{\mathbf{I}} \right]. \end{aligned} \quad (1.54)$$

Because this depends upon the wave state it is a non-linear operator.

The second derivative gives the entropy fluctuation operator,

$$\begin{aligned} \hat{S}''_r(\psi, t) &\equiv \frac{\partial S_r(\psi, t)}{\partial | \psi \rangle \partial \langle \psi |} \\ &= k_B \left[\frac{e^{\hat{S}_r(t)/k_B}}{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle} - \frac{1}{\langle \psi | \psi \rangle} \hat{\mathbf{I}} \right] \\ &\quad - k_B \frac{e^{\hat{S}_r(t)/k_B} | \psi \rangle \langle \psi | e^{\hat{S}_r(t)/k_B}}{\langle \psi | e^{\hat{S}_r(t)/k_B} | \psi \rangle^2} + k_B \frac{| \psi \rangle \langle \psi |}{\langle \psi | \psi \rangle^2}. \end{aligned} \quad (1.55)$$

This is also a non-linear operator.

These are to be evaluated on the most likely trajectory, $\bar{\psi}(t)$, which lies in the ground state sub-space, $\hat{S}_r(t)|\bar{\psi}(t)\rangle = S_0(t)|\bar{\psi}(t)\rangle$. In the ground state, the final two terms cancel and the fluctuation operator becomes

$$\begin{aligned} \hat{\bar{S}}''_r(t) &\equiv \hat{S}''_r(\bar{\psi}(t), t) \\ &= \frac{k_B}{N(\bar{\psi}(t))} \left[\frac{e^{\hat{S}_r(t)/k_B}}{e^{S_0(t)/k_B}} - \hat{\mathbf{I}} \right]. \end{aligned} \quad (1.56)$$

This is equal to the entropy force operator also evaluated in the entropy ground state, $\hat{\bar{S}}''_r(t) = \hat{\bar{S}}'_r(t) \equiv \hat{S}'_r(\bar{\psi}(t), t)$. By design, the thermodynamic force vanishes on the most likely trajectory, $\hat{\bar{S}}''_r(t)|\bar{\psi}(t)\rangle = \hat{\bar{S}}'_r(t)|\bar{\psi}(t)\rangle = |0\rangle$, since this has been taken to lie in the ground state sub-space.

Since the most likely trajectory lies in the ground state sub-space, $S_r(\bar{\psi}(t), t)$ is a maximum. Hence one can expand the entropy to quadratic order about the most likely trajectory, which is just fluctuation theory. Recalling the definition of a fluctuation as the departure from the most likely trajectory, $|\phi(t)\rangle \equiv |\psi - \bar{\psi}(t)\rangle$, the (first) entropy in fluctuation form is

$$S_r(\psi, t) = \bar{S}_r(t) + \langle \phi | \hat{\bar{S}}''_r(t) | \phi \rangle + \mathcal{O}(\phi^3). \quad (1.57)$$

It is most useful in this case to take $|\bar{\psi}(t)\rangle = \hat{\mathcal{P}}_0(t)|\psi\rangle$. The linear terms, which correspond to the thermodynamic force, vanish because this is an expansion about the ground state.

Differentiating this expression and comparing it to the derivative above, one can write the thermodynamic force for the wave state ψ in several equivalent ways,

$$\frac{\partial S_r(\psi, t)}{\partial \langle \psi |} = \hat{\bar{S}}''_r(t) | \phi \rangle = \hat{\bar{S}}'_r(t) | \psi \rangle = \hat{\bar{S}}'_r(t) | \psi \rangle. \quad (1.58)$$

These neglect terms $\mathcal{O}(\phi^2)$.

4. Static Entropy Force Operator

In the classical version of the non-equilibrium theory, it was found fruitful, both conceptually and computationally, to replace the full entropy fluctuation matrix by the static part of the entropy fluctuation matrix.³ A similar replacement will be explored here, although it is not required until Eq. (2.24) below.

It will be recalled that the entropy operator is the sum of a static part and a dynamic part,

$$\hat{S}_r(t) = \hat{S}_{st}(t) + \hat{S}_{dyn}(t). \quad (1.59)$$

Since the expectation entropy is a linear function of the entropy operator, it can also be written as the sum of static and dynamic parts. However, as mentioned above, it is the entropy $S_r(\psi, t)$ rather than the entropy expectation value $S_r^{<>}(\psi, t)$ that features in the reduction condition and that will appear in the stochastic, dissipative equation of motion. The entropy is a non-linear function of the entropy operator, and it is not possible to split it into pure static and dynamic parts. One can however *define* the static part of the entropy to be

$$S_{st}(\psi, t) \equiv S_r(\psi, t, [\hat{S}_{dyn} \equiv 0]), \quad (1.60)$$

and the dynamic part to be the remainder

$$S_{dyn}(\psi, t) \equiv S_r(\psi, t) - S_{st}(\psi, t). \quad (1.61)$$

Note that the dynamic part contains static contributions, $S_{dyn}(\psi, t) \neq S_r(\psi, t, [\hat{S}_{st} \equiv 0])$.

As mentioned above, in the classical case it was found useful to replace the full entropy fluctuation matrix by the static part of the entropy fluctuation matrix.³ In the present case, the analogous replacement is

$$\hat{\bar{S}}''_r(t) \approx \hat{\bar{S}}''_{st}(t), \quad (1.62)$$

where the static part of the entropy fluctuation operator is defined to be

$$\hat{\bar{S}}''_{st}(t) \equiv \hat{\bar{S}}'_{st}(t) \equiv \frac{k_B}{N(\bar{\psi}(t))} \left[\frac{e^{\hat{S}_{st}(t)/k_B}}{e^{S_0(t)/k_B}} - \hat{\mathbf{I}} \right]. \quad (1.63)$$

Note that here and below the over line signifies quantities evaluated in the ground state of the entropy, not the

ground state of the static part of the entropy. Specifically, $\hat{S}_r(t)|\bar{\psi}(t)\rangle = S_0(t)|\bar{\psi}(t)\rangle$. This is the reason that it is $S_0(t)$, not $S_0^{\text{st}}(t)$, that appears in this definition of $\hat{S}_{\text{st}}'(t)$. Note that this latter operator is not guaranteed to be negative definite, but one nevertheless expects it to be at least approximately so.

The preceding equation gives the first and second derivatives of the static part of the entropy evaluated in the reservoir entropy ground state. This is precisely what is required for the fluctuation expansion of the static part of the entropy about the entropy ground state,

$$S_{\text{st}}(\psi, t) = \bar{S}_{\text{st}}(t) + \langle \bar{\psi}(t) | \hat{S}_{\text{st}}'(t) | \phi \rangle + \langle \phi | \hat{S}_{\text{st}}'(t) | \bar{\psi}(t) \rangle + \langle \phi | \hat{S}_{\text{st}}''(t) | \phi \rangle + \mathcal{O}(\phi^3). \quad (1.64)$$

The linear terms do not vanish because the point of expansion, $\bar{\psi}(t)$, is not a maximum of the static entropy operator. Combining this with the fluctuation expansion of the entropy, Eq. (1.57), then by definition the dynamic part of the reservoir entropy has expansion

$$\begin{aligned} S_{\text{dyn}}(\psi, t) &\equiv S_r(\psi, t) - S_{\text{st}}(\psi, t) \\ &= \bar{S}_r(t) - \bar{S}_{\text{st}}(t) - \langle \bar{\psi}(t) | \hat{S}_{\text{st}}'(t) | \phi \rangle \\ &\quad - \langle \phi | \hat{S}_{\text{st}}'(t) | \bar{\psi}(t) \rangle + \mathcal{O}(\phi^3). \end{aligned} \quad (1.65)$$

The quadratic terms cancel upon using the above replacement, $\hat{S}_r''(t) \approx \hat{S}_{\text{st}}''(t)$. Hence the dynamic part of the thermodynamic force is to leading order constant in the excited sub-space of wave space,

$$\frac{\partial S_{\text{dyn}}(\psi, t)}{\partial \langle \psi |} = -\hat{S}_{\text{st}}'(t) | \bar{\psi}(t) \rangle + \mathcal{O}(\phi^2). \quad (1.66)$$

This is entirely analogous to the classical result (see Eq. (8.26) of Ref. [3], or Eq. (20) of Ref. [4]). This is only constant as far as the excited sub-space is concerned, since $|\bar{\psi}(t)\rangle = \hat{P}_0(t)|\psi\rangle$.

Differentiating these two fluctuation forms, the consequent thermodynamic force is

$$\begin{aligned} \frac{\partial S_r(\psi, t)}{\partial \langle \psi |} &= \hat{S}_{\text{st}}'(t) | \bar{\psi}(t) \rangle + \hat{S}_{\text{st}}''(t) | \phi \rangle - \hat{S}_{\text{st}}'(t) | \bar{\psi}(t) \rangle \\ &= \hat{S}_{\text{st}}''(t) | \phi \rangle \\ &= \hat{S}_{\text{st}}'(t) \hat{P}_{\perp}(t) | \psi \rangle. \end{aligned} \quad (1.67)$$

The neglected terms here are of quadratic order in the fluctuation. The penultimate equality could have been written down directly by making the static fluctuation operator replacement, Eq. (1.62), in the original fluctuation expansion of the entropy, Eq. (1.57), and differentiating. Part of the point of the exercise, however, was to explore the implications for the dynamic part of the entropy, and also to show the consonance with the classical results. Additionally, it gives certainty about the exact form for the static fluctuation operator, which is always desirable. The final equality uses the fact that

$\hat{S}_{\text{st}}''(t) = \hat{S}_{\text{st}}'(t)$. It also assumes that $|\bar{\psi}(t)\rangle = \hat{P}_0(t)|\psi\rangle$. This form will prove useful in Eq. (2.24) *et seq.* below.

Using the static part of the fluctuation operator in place of the full fluctuation operator, Eq. (1.62), might appear to be an approximation, but several justifications can be offered. In the first place, fluctuations about the non-equilibrium state are determined by the current molecular structure, and that these fluctuations have the same symmetries as equilibrium fluctuations. There is an abundance of computer simulation data for classical system that show that the fluctuations in a non-equilibrium system are identical to those in the corresponding local equilibrium system.^{1,2,45,46} Further, this replacement appears necessary on physical grounds, namely that in the dissipative Schrödinger equation, this term comes from the reservoir-sub-system interactions and it is the static part of the entropy operator that fully reflects such interactions (c.f. the discussion in the conclusion of Ref. [4]). Finally, the point entropy derived above is based upon the average trajectory (more precisely, the average of the square of the stochastic propagator), and its gradient gives the difference in this average value. What is required for the dissipative Schrödinger equation, is the change in reservoir entropy on an actual trajectory, and this is given exactly by the gradient in the static part of the entropy. This matter is further discussed at the end of §II C below.

II. TRANSITIONS AND MOTION IN WAVE SPACE

A. Second Entropy and the Most Likely Transition

The second entropy is the entropy for transitions. Accordingly, maximizing it determines the most likely trajectory and gives the most likely propagator. In §3A of Paper II⁸ and in §3 of Paper III⁹ of the present series, the second entropy for the quantum equilibrium case was analyzed. The present non-equilibrium case utilizes the same analysis and notation, the main difference being that microscopic reversibility does not here hold. The approach that follows is essentially the quantum version of the non-equilibrium classical analysis given in §8.3.2 of Ref. [3] or §§IIB and III of Ref. [4].

The focus is on the transition $\{\psi_1, t_1\} \rightarrow \{\psi_2, t_2\}$. If $t_2 > t_1$, then this is a physical transition, (i.e. it answers the question—where will the system go to?), and if $t_2 < t_1$, then this is a mathematical transition, (i.e. it answers the question—where did the system come from?).

Recall that the fluctuation of the sub-system wave function is $\phi(t) \equiv \psi(t) - \bar{\psi}(t)$. In the above, the most likely trajectory was taken to be the ground state projection of the current wave function, $|\bar{\psi}(t)\rangle = \hat{P}_0(t)|\psi\rangle$. However the above dealt with one-time quantities, and here the concern is with two-time quantities, so some care is required. Here the most likely trajectory at the initial time is taken to be the ground state projection of

the initial wave function, $|\bar{\psi}(t_1)\rangle = \hat{\mathcal{P}}_0(t_1)|\psi_1\rangle$, and at the final time it is taken to be the most likely evolution of this, $|\bar{\psi}(t_2)\rangle = \hat{\mathcal{U}}_{t_2, t_1}|\bar{\psi}(t_1)\rangle$. (The outcome of this section will be the explicit form for the time propagator.) Hence the fluctuations are

$$\begin{aligned} |\phi_1\rangle &\equiv |\psi_1\rangle - \hat{\mathcal{P}}_0(t_1)|\psi_1\rangle, \\ \text{and } |\phi_2\rangle &\equiv |\psi_2\rangle - \hat{\mathcal{U}}_{t_2, t_1}\hat{\mathcal{P}}_0(t_1)|\psi_1\rangle. \end{aligned} \quad (2.1)$$

It is not necessary to formulate these in a more symmetric fashion, as the symmetry of the quadratic form given next will shortly be broken. It is to be noted that ϕ_1 lies entirely in the excited state, and, since $|t_{21}| \rightarrow 0$, it is also true that $\bar{\psi}(t_2)$ is either fully or predominantly in the ground state. It is actually $\bar{\psi}(t_1)$ rather than $\bar{\psi}(t_2)$ that must lie in the ground state because the non-linear thermodynamic force operator that is required below is evaluated at t_1 and at $|\bar{\psi}(t_1)\rangle = \hat{\mathcal{P}}_0(t_1)|\psi_1\rangle$.

Assume that the second entropy for the transition has the quadratic fluctuation form

$$\begin{aligned} S^{(2)}(\psi_2, t_2; \psi_1, t_1) &= \langle \phi_2 | \hat{a}(t_{21}, t) | \phi_2 \rangle + \langle \phi_1 | \hat{c}(t_{21}, t) | \phi_1 \rangle \\ &\quad + \langle \phi_2 | \hat{b}(t_{21}, t) | \phi_1 \rangle + \langle \phi_1 | \hat{b}(t_{21}, t)^\dagger | \phi_2 \rangle \\ &\quad + \frac{1}{2} [\bar{S}_r(t_2) + \bar{S}_r(t_1)]. \end{aligned} \quad (2.2)$$

Here $t \equiv [t_1 + t_2]/2$ is the midpoint, and $t_{21} \equiv t_2 - t_1$ is the first time in the argument minus the second. Usually the time argument t will be suppressed. The first entropies that appear here are $\bar{S}_r(t_i) \equiv S_r(\bar{\psi}(t_i), t_i)$, $i = 1, 2$, which are equal either exactly or approximately to the ground state entropy $S_0(t_i)$.

The origin of the final time-dependent constant is derived in §8.3.1 of Ref. [3] and in §4 of Ref. [9]. (The analogous constant was neglected in transforming the trajectory entropy operator to the point entropy operator, Eq. (1.33), as was discussed in the final paragraph of §IC 2.) It is related to the reduction condition,^{3,39} which for the conditionally most likely state $\bar{\psi}_2 \equiv \bar{\psi}(t_2|\psi_1, t_1)$ is

$$S^{(2)}(\bar{\psi}_2, t_2; \psi_1, t_1) = S_r(\psi_1, t_1) + [\bar{S}_r(t_2) - \bar{S}_r(t_1)]/2. \quad (2.3)$$

This corresponds to Eq. (8.38) of Ref. [3] and to Eq. (4.4) of Ref. [9]. As shown in Ref. [9], the reduction condition applies to the entropy, not the expectation entropy.

The second entropy must reflect statistical symmetry, $S^{(2)}(\psi_2, t_2; \psi_1, t_1) = S^{(2)}(\psi_1, t_1; \psi_2, t_2)$. Hence

$$\hat{a}(t_{12}) = \hat{c}(t_{21}), \text{ and } \hat{b}(t_{12}) = \hat{b}(t_{21})^\dagger. \quad (2.4)$$

The second entropy must be real, $S^{(2)}(\psi_2, t_2; \psi_1, t_1)^* = S^{(2)}(\psi_2, t_2; \psi_1, t_1)$. Hence

$$\hat{a}(t_{21}) = \hat{a}(t_{21})^\dagger, \text{ and } \hat{c}(t_{21}) = \hat{c}(t_{21})^\dagger, \quad (2.5)$$

which is to say that they are self-adjoint. The cross-term is real by design.

These symmetries also held in the equilibrium quantum case treated in §3A of Paper II.⁸ The only symmetry that does not hold in the present non-equilibrium case is microscopic reversibility. Hence much of the analysis of §3A⁸ holds also here.

In detail, since $\bar{\psi}_2 \rightarrow \psi_1$ as $|t_{21}| \rightarrow 0$, the second entropy must contain essentially a δ -function singularity. Hence the small $|t_{21}|$ expansions must be of the form

$$\hat{a}(\tau) = \frac{1}{|t_{21}|}\hat{a}_{-1} + \frac{1}{t_{21}}\hat{a}'_{-1} + \hat{a}_0 + \hat{\tau}\hat{a}'_0 + \mathcal{O}(t_{21}), \quad (2.6)$$

$$\hat{b}(t_{21}) = \frac{1}{|t_{21}|}\hat{b}_{-1} + \frac{1}{t_{21}}\hat{b}'_{-1} + \hat{b}_0 + \hat{\tau}\hat{b}'_0 + \mathcal{O}(t_{21}), \quad (2.7)$$

and

$$\hat{c}(t_{21}) = \frac{1}{|t_{21}|}\hat{c}_{-1} + \frac{1}{t_{21}}\hat{c}'_{-1} + \hat{c}_0 + \hat{\tau}\hat{c}'_0 + \mathcal{O}(t_{21}), \quad (2.8)$$

with $\hat{\tau} \equiv \text{sign } t_{21} = t_{21}/|t_{21}|$.

The reason why the non-analytic terms appear (i.e. those containing $|t_{21}|$ and $\hat{\tau}$) is that these are necessary to yield the irreversible behavior that is characteristic of all thermodynamic evolution. One concludes that this is not a Taylor expansion for an infinitesimal time step, since this would only ever yield analytic terms, but rather an expansion for small but finite time steps that is a resummation of an infinite order Taylor expansion. The validity of beginning the expansion with terms $\mathcal{O}(t_{21}^{-1})$ can be judged by the consequences; amongst other things it yields a physically plausible stochastic Schrödinger equation with a conventional velocity for the wave function.

From the symmetries given above, $\hat{a}(t_{21}) = \hat{a}(t_{21})^\dagger$, and $\hat{a}(t_{21}) = \hat{c}(-t_{21})$, one can see that the unprimed \hat{a} are self-adjoint and equal the unprimed \hat{c} , and the primed \hat{a} are self-adjoint and equal the negative of the primed \hat{c} . Also, since $\hat{b}(t_{21}) = \hat{b}(-t_{21})^\dagger$, the unprimed \hat{b} are self-adjoint, and the primed \hat{b} are anti-self-adjoint. (In quantum mechanics, the words Hermitian operator and self-adjoint operator are used synonymously.)¹¹

Since $\bar{\psi}_2 \rightarrow \psi_1$ as $|t_{21}| \rightarrow 0$, to leading order $\hat{a}(t_{21}) = -\hat{b}(t_{21})$, which implies that

$$\hat{a}_{-1} = -\hat{b}_{-1} \equiv -\hat{\lambda}^{-1}, \text{ and } \hat{a}'_{-1} = -\hat{b}'_{-1} = \hat{0}. \quad (2.9)$$

From the symmetry relations, $\hat{\lambda}$ is an Hermitian operator that is positive definite (because the second entropy must be negative definite). For reasons that will become clear shortly, this will be called the dissipative operator, although it could equally well be called the drag operator, or the friction operator. The primed coefficients individually vanish because \hat{a}'_{-1} is self-adjoint and \hat{b}'_{-1} is anti-self-adjoint. With these, the small time expansions read

$$\hat{a}(t_{21}) = \frac{-1}{|t_{21}|}\hat{\lambda}^{-1} + \hat{a}_0 + \hat{\tau}\hat{a}'_0 + \mathcal{O}(t_{21}), \quad (2.10)$$

$$\hat{b}(t_{21}) = \frac{1}{|t_{21}|} \hat{\lambda}^{-1} + \hat{b}_0 + \hat{\tau} \hat{b}'_0 + \mathcal{O}(t_{21}), \quad (2.11)$$

and

$$\hat{c}(t_{21}) = \frac{-1}{|t_{21}|} \hat{\lambda}^{-1} + \hat{a}_0 - \hat{\tau} \hat{a}'_0 + \mathcal{O}(t_{21}). \quad (2.12)$$

Here $\hat{\lambda}$, \hat{a}_0 , \hat{a}'_0 , and \hat{b}_0 are Hermitian, and \hat{b}'_0 is anti-Hermitian. These all depend upon t (not shown).

Maximizing the second entropy by setting its derivative with respect to $\langle \phi_2 |$ to zero, one obtains the conditional most likely state as

$$\begin{aligned} |\bar{\phi}_2\rangle &= -\hat{a}(t_{21})^{-1} \hat{b}(t_{21}) |\phi_1\rangle \\ &= |\phi_1\rangle + t_{21} \hat{\lambda} [\hat{a}'_0 + \hat{b}'_0] |\phi_1\rangle + |t_{21}| \hat{\lambda} [\hat{a}_0 + \hat{b}_0] |\phi_1\rangle \\ &\quad + \mathcal{O}(t_{21}^2). \end{aligned} \quad (2.13)$$

The left hand side is more precisely written $|\bar{\phi}(t_{21}|\phi_1, t)\rangle$.

From the reduction condition Eq. (2.3) and the fluctuation expression Eq. (1.57) one has

$$\begin{aligned} S^{(2)}(\bar{\psi}_2, t_2; \psi_1, t_1) &= S_r(\psi_1, t_1) + \frac{1}{2} [\bar{S}_r(t_2) - \bar{S}_r(t_1)] \\ &= \langle \phi_1 | \hat{S}_r''(t_1) | \phi_1 \rangle \\ &\quad + \frac{1}{2} [\bar{S}_r(t_2) + \bar{S}_r(t_1)]. \end{aligned} \quad (2.14)$$

Evaluating the left hand side using the preceding expression for $|\bar{\phi}_2\rangle$ and its conjugate $\langle \bar{\phi}_2|$ in the fluctuation expression for the second entropy, Eq. (2.2), one sees that the constant term in the final equality here equals the constant term in the second entropy, Eq. (2.2). What remains on the left hand side is the expectation value of an operator (that is a function of $\hat{a}(t_{21})$, $\hat{b}(t_{21})$, and $\hat{c}(t_{21})$) in the wave state ϕ_1 , which when set equal to the same expectation value on the final equality here yields the explicit reduction condition

$$\hat{c}(t_{21}, t) - \hat{b}(t_{21}, t)^\dagger \hat{a}(t_{21}, t)^{-1} \hat{b}(t_{21}, t) = \hat{S}_r''(t_1). \quad (2.15)$$

The left hand side is clearly Hermitian, as it must be. This equality has to hold for all values of t_2 . Since this is formally identical to the corresponding equilibrium result, the small time expansion given in Eq. (3.21) of Ref. [8] must hold, and so the expansion coefficients of the operators must reduce to

$$\hat{a}_0(t) + \hat{b}_0(t) = \frac{1}{2} \hat{S}_r''(t) = \frac{1}{2} \hat{S}_r'(t). \quad (2.16)$$

Recall from Eq. (1.56) that in the ground state, the entropy fluctuation operator equals the entropy force operator, $\hat{S}_r''(t) = \hat{S}_r'(t) \equiv \hat{S}'_r(\bar{\psi}(t), t)$.

With this result, the irreversible operator (i.e. the operator proportional to $|t_{21}|$) for the most likely evolution of the fluctuation, Eq. (2.13), is

$$|t_{21}| \hat{\lambda}(t) [\hat{a}_0(t) + \hat{b}_0(t)] = \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_r(t). \quad (2.17)$$

When this is inserted into the evolution equation Eq. (2.13), one sees that the irreversible term includes the factor $\hat{S}_r'(t) |\phi_1\rangle = \hat{S}_r'(t) |\psi_1\rangle$. This is the thermodynamic force or entropy gradient, Eq. (1.58). This term drives the current wave state of the sub-system, ψ_1 , toward the ground state. This term ultimately gives the change in entropy during the transition, which is the origin of the name ‘dissipative operator’ for $\hat{\lambda}(t)$.

As in the equilibrium case treated in Paper II (see Eq. (3.32) of Ref. [8]) the reversible term in Eq. (2.13) (the one proportional to t_{21}) must contain the adiabatic evolution,

$$t_{21} \hat{\lambda} [\hat{a}'_0 + \hat{b}'_0] = \frac{t_{21}}{i\hbar} \hat{\mathcal{H}}(t). \quad (2.18)$$

Any reversible reservoir contribution is expected to be negligible compared to this. For completeness, the Hermitian conjugate of this is

$$[\hat{a}'_0 - \hat{b}'_0] \hat{\lambda} = \frac{-1}{i\hbar} \hat{\mathcal{H}}(t). \quad (2.19)$$

B. Dissipative Schrödinger Equation

With these results the conditional most likely fluctuation is

$$\begin{aligned} |\bar{\phi}_2\rangle &= -\hat{a}(t_{21})^{-1} \hat{b}(t_{21}) |\phi_1\rangle \\ &= |\phi_1\rangle + t_{21} \hat{\lambda} [\hat{a}'_0 + \hat{b}'_0] |\phi_1\rangle + |t_{21}| \hat{\lambda} [\hat{a}_0 + \hat{b}_0] |\phi_1\rangle \\ &= |\phi_1\rangle + \frac{t_{21}}{i\hbar} \hat{\mathcal{H}}(t) |\phi_1\rangle + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_r(t) |\phi_1\rangle. \end{aligned} \quad (2.20)$$

The neglected terms are $\mathcal{O}(t_{21}^2)$.

From this one can identify one form for the most likely time propagator, namely

$$\hat{\mathcal{U}}_{ne}(t_2, t_1) = \hat{\mathbb{I}} + \frac{t_{21}}{i\hbar} \hat{\mathcal{H}}(t) + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_r(t). \quad (2.21)$$

This gives the conditional most likely wave state as

$$\begin{aligned} |\bar{\psi}(t_2|\psi_1, t_1)\rangle &= \hat{\mathcal{U}}_{ne}(t_2, t_1) |\psi_1\rangle \\ &= |\psi_1\rangle + \frac{t_{21}}{i\hbar} \hat{\mathcal{H}}(t) |\psi_1\rangle \\ &\quad + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_r(t) |\psi_1\rangle, \end{aligned} \quad (2.22)$$

and the evolution of the ground state projection as

$$\begin{aligned} |\bar{\psi}(t_2)\rangle &= \hat{\mathcal{U}}_{ne}(t_2, t_1) |\bar{\psi}(t_1)\rangle \\ &= |\bar{\psi}(t_1)\rangle + \frac{t_{21}}{i\hbar} \hat{\mathcal{H}}(t) |\bar{\psi}(t_1)\rangle. \end{aligned} \quad (2.23)$$

The evolution of the ground state projection is purely adiabatic because the thermodynamic force vanishes in the ground state, Eq. (1.58), $\hat{S}'_r(t) |\bar{\psi}(t_1)\rangle =$

$\hat{S}'_r(t) \hat{P}_0(t) |\psi_1\rangle = |0\rangle$. In general the propagator, Eq. (2.21), does not couple the sub-system ground state to the reservoir.

Alternatively, using the results of §ID 4, the thermodynamic force can be replaced by its static part. Writing the fluctuation explicitly in terms of wave states, Eq. (2.20) becomes

$$\begin{aligned} & |\bar{\psi}(t_2|\psi_1, t_1)\rangle - |\bar{\psi}(t_2)\rangle \\ &= |\psi_1\rangle + \frac{t_{21}}{i\hbar} \hat{H}(t) |\psi_1\rangle + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_{st}(t) \hat{P}_\perp(t) |\psi_1\rangle \\ &\quad - |\bar{\psi}(t_1)\rangle - \frac{t_{21}}{i\hbar} \hat{H}(t) |\bar{\psi}(t_1)\rangle, \end{aligned} \quad (2.24)$$

where the excited state projection is $\hat{P}_\perp(t) \equiv \hat{I} - \hat{P}_0(t)$. This expresses the thermodynamic force in terms of the static part of the entropy fluctuation operator, Eq. (1.67), $\hat{S}'_r(t) |\psi_1\rangle = \hat{S}'_{st}(t) \hat{P}_\perp(t) |\psi_1\rangle$. Since the starting point of the most likely trajectory was chosen as $|\bar{\psi}(t_1)\rangle = \hat{P}_0(t_1) |\psi_1\rangle$, and since the end point was $|\bar{\psi}(t_2)\rangle = \hat{U}(t_2, t_1) |\bar{\psi}(t_1)\rangle$, one can identify from this the most likely time propagator

$$\hat{U}(t_2, t_1) = \hat{I} + \frac{t_{21}}{i\hbar} \hat{H}(t) + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_{st}(t) \hat{P}_\perp(t). \quad (2.25)$$

This gives the most likely wave state following the transition as

$$\begin{aligned} |\bar{\psi}(t_2|\psi_1, t_1)\rangle &= \hat{U}(t_2, t_1) |\psi_1\rangle \\ &= |\psi_1\rangle + \frac{t_{21}}{i\hbar} \hat{H}(t) |\psi_1\rangle \\ &\quad + \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_{st}(t) \hat{P}_\perp(t) |\psi_1\rangle, \end{aligned} \quad (2.26)$$

and the evolution of the ground state projection as

$$\begin{aligned} |\bar{\psi}(t_2)\rangle &= \hat{U}(t_2, t_1) |\bar{\psi}(t_1)\rangle \\ &= |\bar{\psi}(t_1)\rangle + \frac{t_{21}}{i\hbar} \hat{H}(t) |\bar{\psi}(t_1)\rangle. \end{aligned} \quad (2.27)$$

Again, in general there is no contribution from the ground state to the reservoir-induced evolution. There may be contributions from the excited states to the reservoir-induced evolution of the ground state. Also, the Hamiltonian operator for the adiabatic evolution may mix ground and excited states.

The trajectory due to the present dissipative propagator, $\hat{U}_{ne}(t_2, t_1) \approx \hat{U}(t_2, t_1)$, corrects the corresponding classical^{3,4} and equilibrium quantum⁸ cases in that here there is no reversible reservoir contribution (i.e. here there is no reservoir term proportional to t_{21}). In earlier work the fluctuations were from ‘the’ most likely trajectory, which was argued to be reversible.^{3,4,8} Here the fluctuations are from the ground state projection, and reversibility does not come into it. A further argument for preferring the present formulation is that the derivation of the adiabatic part of the evolution, Eq. (2.18),

neglected any reversible reservoir contribution contained in the term $\hat{\lambda}(t)[\hat{a}'_0(t) + \hat{b}'_0(t)]$ on the grounds that it was small compared with the reversible adiabatic term itself. It would therefore be a little inconsistent to invoke a reversible reservoir contribution for the evolution of the ground state. Upon reflection, there is no compelling reason to invoke a reversible trajectory or to have different propagators for the ground and for the excited states. In the light of the present results, the analysis in Refs. [3,4,8] needs to be revisited.

The most likely propagator may be written

$$\hat{U}(t_2, t_1) \equiv \hat{I} + \frac{t_{21}}{i\hbar} \hat{H}(t) + \hat{\mathcal{R}}(t_{21}, t) + \mathcal{O}(t_{21}^2), \quad (2.28)$$

with the dissipative reservoir operator being defined as

$$\hat{\mathcal{R}}(t_{21}, t) \equiv \frac{|t_{21}|}{2} \hat{\lambda}(t) \hat{S}'_{st}(t) \hat{P}_\perp(t). \quad (2.29)$$

The static entropy force operator $\hat{S}'_{st}(t)$ depends upon the magnitude of the entropy ground state projection of the wave function, $N(\bar{\psi}(t))$. In this sense the most likely propagator and the dissipative reservoir operator are non-linear operators. However, since this is a constant factor, it at worst re-scales the thermodynamic force, and so the non-linearity is weak and unimportant. In fact, it could be incorporated in the dissipative operator, $\hat{\lambda}(t)$, which can be arbitrarily scaled by a positive number.

As mentioned in §ID 4, rewriting of the thermodynamic force in terms of the static part of the thermodynamic force is effectively the same as replacing the entropy fluctuation operator by the static part of the entropy fluctuation operator, Eq. (1.62) or (1.67). This might appear to be an approximation, but using the expression (1.66) for the dynamic contribution to the force can be argued to be an exact result.⁴ It appears that the replacement is necessary on physical grounds, namely that in the dissipative Schrödinger equation, the dissipative term comes from the reservoir-sub-system interactions and it is the static part of the entropy operator that fully reflects such interactions (c.f. the discussion in the conclusion of Ref. [4]).

One way to see why this replacement is both necessary and exact is to note the distinction between the change in entropy and the difference in entropy (see §8.4.1 of Ref. [3]). For a transition $\{\psi_1, t_1\} \rightarrow \{\psi_2, t_2\}$, the difference in entropy is $S_r(\psi_2, t_2) - S_r(\psi_1, t_1)$, whereas the change in entropy is $S_{st}(\psi_2, t_2) - S_{st}(\psi_1, t_1) - t_{21} \dot{S}_{st}^0(\psi, t)$. The expression for $S_r(\psi, t)$ is based upon the average trajectory, (more precisely, the average of the square of the propagator), and this is an approximation to the actual entropy on the specific trajectory being considered in the current transition. Hence the difference in entropy is an approximation to the actual change in entropy that occurs in the transition. Since the static part of the entropy is defined via the exchange of conserved quantities with the reservoir, it is exact for such an exchange. Hence

this expression for the change in entropy that involves the static part of the entropy gives exactly the change in entropy for the above transition. This is fundamentally the reason that the above expression for the dissipative Schrödinger equation in terms of the static part of the thermodynamic force is exact.

1. Alternatively

One can incorporate the adiabatic development into the most likely state about which the final terminus fluctuates. That is, choose the reversible reservoir contribution to vanish,

$$t_{21}\hat{\lambda}[\hat{a}'_0 + \hat{b}'_0] = 0, \quad (2.30)$$

and let $|\bar{\psi}(t_1)\rangle = \hat{P}_0(t)|\psi_1\rangle$, and $|\bar{\psi}(t_2)\rangle = |\bar{\psi}(t_1)\rangle + (t_{21}/i\hbar)\hat{H}(t)|\psi_1\rangle$, so that the fluctuations are

$$|\phi_1\rangle \equiv |\psi_1\rangle - \hat{P}_0(t_1)|\psi_1\rangle, \quad (2.31)$$

$$\text{and } |\phi_2\rangle \equiv |\psi_2\rangle - \hat{P}_0(t_1)|\psi_1\rangle - \frac{t_{21}}{i\hbar}\hat{H}(t_1)|\psi_1\rangle.$$

Then one has

$$\begin{aligned} |\bar{\psi}(t_2|\psi_1, t_1)\rangle &= |\bar{\psi}(t_2)\rangle - \hat{a}(t_{21})^{-1}\hat{b}(t_{21})|\phi_1\rangle \\ &= |\bar{\psi}(t_2)\rangle + |\phi_1\rangle + |t_{21}\hat{\lambda}[\hat{a}_0 + \hat{b}_0]|\phi_1\rangle + \mathcal{O}(t_{21}^2) \\ &= |\psi_1\rangle + \frac{t_{21}}{i\hbar}\hat{H}(t)|\psi_1\rangle + \frac{|t_{21}|}{2}\hat{\lambda}(t)\hat{S}'_{\text{st}}(t)|\psi_1\rangle. \\ &= |\psi_1\rangle + \frac{t_{21}}{i\hbar}\hat{H}(t)|\psi_1\rangle + \frac{|t_{21}|}{2}\hat{\lambda}(t)\hat{S}'_{\text{st}}(t)\hat{P}_{\perp}(t_1)|\psi_1\rangle. \end{aligned} \quad (2.32)$$

Although the final result is the same as the above, the physical interpretation is better because the fluctuations should be the random contribution from the reservoir.

C. Stochastic, Dissipative Schrödinger Equation

Since the evolution of the sub-system wave function is determined in part by the interactions with the reservoir, and since the wave function of the reservoir is indeterminate, there must be a random element to the evolution. This means that the evolution is only determined in a probabilistic sense; each time that the sub-system visits a particular sub-system wave state the subsequent evolution is not exactly the same. This random reservoir propagator acts on the sub-system and it can be decomposed into the average (or most likely) part, and the stochastic (or fluctuation) part,

$$\hat{\mathcal{R}}(t_{21}, t) = \hat{\bar{\mathcal{R}}}(t_{21}, t) + \hat{\mathcal{R}}(t_{21}, t). \quad (2.33)$$

The most likely part is the dissipative reservoir operator given above. The stochastic operator obviously has

zero mean, $\langle \hat{\mathcal{R}}(t_{21}, t) \rangle_{\text{stoch}} = 0$. Adding this stochastic reservoir contribution to the above deterministic equation gives the stochastic, dissipative Schrödinger equation,

$$\begin{aligned} |\psi(t_2)\rangle &= \left[\hat{\mathbf{I}} + \frac{t_{21}}{i\hbar}\hat{H}(t) + \hat{\bar{\mathcal{R}}}(t_{21}, t) + \hat{\mathcal{R}}(t_{21}, t) \right] |\psi(t_1)\rangle \\ &\equiv \left[\hat{\bar{\mathcal{U}}}(t_2, t_1) + \hat{\mathcal{R}}(t_{21}, t) \right] |\psi(t_1)\rangle \\ &\equiv \hat{\mathcal{U}}(t_2, t_1) |\psi(t_1)\rangle. \end{aligned} \quad (2.34)$$

The first neglected term here is $\mathcal{O}(t_{21}^2)$. The stochastic operator $\hat{\mathcal{R}}(t_{21}, t)$ and the dissipative (or drag) operator $\hat{\lambda}(t)$ must be such that the unitary condition, Eq. (1.17), and possibly also the stationarity condition, Eq. (1.19), are satisfied.

The unitary condition, Eq. (1.17), to linear order in the time step is explicitly

$$\begin{aligned} \hat{\mathbf{I}} &= \left\langle \hat{\mathcal{U}}(t_2, t_1)^\dagger \hat{\mathcal{U}}(t_2, t_1) \right\rangle_{\text{stoch}} \\ &= \hat{\mathbf{I}} + \frac{|t_{21}|}{2} \left[\hat{\lambda}(t) \hat{S}'_{\text{st}}(t) \hat{P}_{\perp}(t) + \hat{P}_{\perp}(t) \hat{S}'_{\text{st}}(t) \hat{\lambda}(t) \right] \\ &\quad + \left\langle \hat{\mathcal{R}}(t_{21}, t)^\dagger \hat{\mathcal{R}}(t_{21}, t) \right\rangle_{\text{stoch}}. \end{aligned} \quad (2.35)$$

This uses the fact that $\hat{\lambda}(t)$, $\hat{S}'_{\text{st}}(t)$, and $\hat{P}_{\perp}(t)$ are Hermitian. The adiabatic terms have canceled. This gives for the variance

$$\begin{aligned} &\left\langle \hat{\mathcal{R}}(t_{21}, t)^\dagger \hat{\mathcal{R}}(t_{21}, t) \right\rangle_{\text{stoch}} \\ &= \frac{|t_{21}|}{2} \left[\hat{\lambda}(t) \hat{S}'_{\text{st}}(t) \hat{P}_{\perp}(t) + \hat{P}_{\perp}(t) \hat{S}'_{\text{st}}(t) \hat{\lambda}(t) \right]. \end{aligned} \quad (2.36)$$

Hence if the real, symmetric, dissipative operator $\hat{\lambda}(t)$ is specified, the probability distribution for the random operator is given by this. This is the fundamental quantum fluctuation-dissipation theorem.

The stationarity condition, Eq. (1.19), to linear order in the time step, is explicitly

$$\begin{aligned} \hat{\phi}(t_2) &= \left\langle \hat{\mathcal{U}}(t_1, t_2)^\dagger \hat{\phi}(t_1) \hat{\mathcal{U}}(t_1, t_2) \right\rangle_{\text{stoch}} \\ &= \hat{\phi}(t_1) + \frac{t_{21}}{i\hbar} \left[\hat{H}(t) \hat{\phi}(t_1) - \hat{\phi}(t_1) \hat{H}(t) \right] \\ &\quad + \frac{|t_{21}|}{2} \left[\hat{\phi}(t_1) \hat{\lambda}(t) \hat{S}'_{\text{st}}(t) \hat{P}_{\perp}(t) \right. \\ &\quad \left. + \hat{P}_{\perp}(t) \hat{S}'_{\text{st}}(t) \hat{\lambda}(t) \hat{\phi}(t_1) \right] \\ &\quad + \left\langle \hat{\mathcal{R}}(t_{12}, t)^\dagger \hat{\phi}(t_1) \hat{\mathcal{R}}(t_{12}, t) \right\rangle_{\text{stoch}}. \end{aligned} \quad (2.37)$$

This also gives the evolution of a non-optimum (transient, or approximate) probability operator.

1. Ansatz for the Reservoir Operators

The drag and stochastic operators represent the perturbative interactions of the sub-system with the reservoir. As such they can be freely chosen, provided that

they satisfy the unitary condition. The simplest ansatz involves a single drag coefficient and a single stochastic coefficient. One can take

$$\hat{\lambda}(t) = -\lambda(t) \hat{\mathcal{P}}_{\perp}(t) \hat{\mathcal{S}}'_{\text{st}}(t) \hat{\mathcal{P}}_{\perp}(t), \quad (2.38)$$

and

$$\hat{\mathcal{R}}(t) = r(t) \hat{\mathcal{P}}_{\perp}(t) \hat{\mathcal{S}}'_{\text{st}}(t) \hat{\mathcal{P}}_{\perp}(t), \quad (2.39)$$

with $\lambda(t)$ a positive real number, and $r(t)$ a real random variable. (Recall that $\hat{\lambda}(t)$ is a real, symmetric, positive semi-definite operator, and that $\hat{\mathcal{S}}'_{\text{st}}(t)$ is a real, symmetric, and at least approximately negative semi-definite operator.) The excited state projectors here confine the drag operator and the stochastic operator to the excited sub-space. The reason for doing this is that the operators in the fluctuation form for the second entropy, Eq. (2.2), act on the excited states.

Inserting these into the unitary condition (2.36) one obtains for the variance

$$\langle r(t)^2 \rangle_{\text{stoch}} = |t_{21}| \lambda(t) \quad (2.40)$$

This is the simplest form of the fluctuation-dissipation theorem. It says that the variance of the fluctuations is proportional to the drag coefficient and to the time step.

The non-linearity of the thermodynamic force operator appears as a prefactor that is the magnitude of the ground state projection of the wave function. The non-linearity could be removed by effectively incorporating it into the arbitrary drag coefficient, which is the same as setting $N(\bar{\psi}) = 1$ everywhere.

With the above ansatz in the single step time propagator, the reservoir only couples excited states; during a transition it does not influence, nor is it influenced by the ground state. However, it is likely the adiabatic term mixes ground and excited states.

It should be stressed that this ansatz is offered simply as a possibility worth considering. It has not been tested in practice and the full consequences of using it have not been explored.

D. Density Matrix and Statistical Average

Statistical averages for the non-equilibrium system may be obtained using the stochastic, dissipative Schrödinger equation by constructing the density matrix for the current wave state. Conventionally, a statistical average is obtained from a density matrix that corresponds to a mixture of wave functions, each one a pure quantum state resulting from the collapse of the wave function.^{7,10–12} This is the so-called ensemble approach to statistical mechanics, which is deprecated by the present author. In general the density matrix constructed from a single wave function contains a superposition of states, and so one cannot use it because such

superposition states should not contribute to the statistical average.

In Paper II,⁸ the canonical equilibrium quantum system was analyzed, and the corresponding the stochastic, dissipative Schrödinger equation was used to obtain the statistical average by expressing it as the time average over the trajectory of the density matrix for the current wave state. (It is actually the trace of the product of the density matrix and the operator that occurs.) The reason that this works is that the phase factors of the entropy states are randomly distributed and so averaged over time the superposition states cancel from the density matrix leaving the equivalent of a mixture of pure entropy states as the only non-zero contributions.

One can do something similar in the present non-equilibrium case, except of course that since one wants the average of an operator at a specific time, and since in general the system is time dependent, one cannot take a time average over the trajectory. (For the case of a steady state non-equilibrium system, such as steady heat flow, the sub-system does not change macroscopically with time and it would be possible to take a time average over the trajectory.) Instead of a time average one can construct an average over multiple trajectories.

Let $\psi_a(t)$, $a = 1, 2, \dots, M$, be the wave state at time t given by the a th realization of the stochastic, dissipative Schrödinger equation. If the trajectories are long enough, $t - t_0 \gtrsim \tau_{\text{relax}}$, then the starting wave state is unimportant. One could use the same wave state to start each trajectory, or one could distribute the starting wave states randomly according to the exact or to an approximate probability distribution. The density matrix for the a th trajectory is $\hat{\rho}_a(t) \equiv |\psi_a(t)\rangle \langle \psi_a(t)| / N(\psi_a(t))$, and the statistical average of an operator at time t is

$$\begin{aligned} \langle \hat{O}(t) \rangle_{\text{stat}} &= \frac{1}{M} \sum_{a=1}^M \text{TR} \{ \hat{\rho}_a(t) \hat{O}(t) \} \\ &= \frac{1}{M} \sum_{a=1}^M \frac{\langle \psi_a(t) | \hat{O}(t) | \psi_a(t) \rangle}{\langle \psi_a(t) | \psi_a(t) \rangle}. \end{aligned} \quad (2.41)$$

Although this appears to include superposition states, only pure entropy quantum states contribute to this when the average is taken provided that the magnitudes of the entropy wave states have converged to a value independent of the initial value, and the phase factors of the entropy states are uncorrelated.

For example, in terms of the eigenstates of the entropy operator, $\hat{S}_r(t) |\zeta_{\alpha h}^S(t)\rangle = S_{\alpha}(t) |\zeta_{\alpha h}^S(t)\rangle$, suppose that for $t - t_0 \gtrsim \tau_{\text{relax}}$, the wave function for the a th trajectory has representation

$$|\psi_a(t)\rangle = \sum_{\alpha h} |\psi_{\alpha h}^S(t)\rangle e^{i\theta_{a;\alpha h}(t)} |\zeta_{\alpha h}^S(t)\rangle. \quad (2.42)$$

That is, the amplitude is independent of the particular trajectory. The entropy representation is special in this regard. With this and assuming all wave functions have

the same normalization, the average of the expectation value is explicitly

$$\begin{aligned}
& \frac{1}{M} \sum_{a=1}^M \langle \psi_a(t) | \hat{O}(t) | \psi_a(t) \rangle \\
&= \frac{1}{M} \sum_{a=1}^M \sum_{\alpha,h} \sum_{\beta,g} |\psi_{\alpha h}^S(t)| |\psi_{\beta g}^S(t)| \\
&\quad \times e^{-i[\theta_{a;\alpha h}(t) - \theta_{a;\beta g}(t)]} O_{\alpha h, \beta g}^S(t) \\
&= \sum_{\alpha,h} |\psi_{\alpha h}^S(t)|^2 O_{\alpha h, \alpha h}^S(t). \tag{2.43}
\end{aligned}$$

The random phase factors have ensured that the off-diagonal terms in the entropy representation have averaged to zero,

$$\frac{1}{M} \sum_{a=1}^M e^{-i[\theta_{a;\alpha h}(t) - \theta_{a;\beta g}(t)]} = \delta_{\alpha\beta} \delta_{gh}. \tag{2.44}$$

This leaves an expression that is equivalent to a mixture of pure entropy states. Provided that the distribution of the magnitudes converges to the representation of the probability operator, $|\psi_{\alpha h}^S(t)|^2 \propto \wp_{\alpha,\alpha}^S(t)$, then this is equal to the statistical average that would be obtained directly from the probability operator. One expects that this would be the case if the stochastic, dissipative propagator satisfies the stationarity condition, Eq. (1.19), since it is then plausible that the non-equilibrium probability operator is stable under the action of the propagator.

E. Dynamic Part of the Entropy Operator

It will be recalled that the probability operator for the non-equilibrium system was the exponential of the reservoir entropy operator, which was the sum of static and dynamic parts, Eq. (1.41), $\hat{S}_r(t) = \hat{S}_{st}(t) + \hat{S}_{dyn}(t)$. The dynamic part of the entropy operator was given by Eq. (1.37)

$$\hat{S}_{dyn}(t) = - \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger \hat{S}_{st}^0(t') \hat{U}(t', t) \right\rangle_{stoch}. \tag{2.45}$$

Because $t \geq t'$, here $\hat{U}(t', t)$ is the backward stochastic, dissipative propagator.

In the classical non-equilibrium case, it was shown that the dynamic part of the entropy could be replaced by its odd parity projection, and that the stochastic, dissipative backward trajectories that appeared could be replaced by adiabatic backward trajectories.^{3,4} In the present non-equilibrium quantum case, one may similarly argue that the even parity projection of the entropy operator is dominated by the static entropy operator, which is of course real. Since the feature that distinguishes a non-equilibrium system from its equilibrium counterpart is that the probability operator cannot be real, it follows

that one must retain, and that one need only retain, the odd parity projection of the dynamic entropy operator,

$$\hat{S}_r(t) \approx \hat{S}_{st}(t) + \hat{S}_{dyn}^{odd}(t). \tag{2.46}$$

The odd parity projection is

$$\begin{aligned}
\hat{S}_{dyn}^{odd}(t) &\equiv \frac{1}{2} [\hat{S}_{dyn}(t) - \hat{S}_{dyn}(t)^*] \\
&= \frac{-1}{2} \int_0^t dt' \left[\left\langle \hat{U}(t', t)^\dagger \hat{S}_{st}^0(t') \hat{U}(t', t) \right\rangle_{stoch} \right. \\
&\quad \left. - \left\langle \hat{U}(t', t)^T \hat{S}_{st}^0(t')^* \hat{U}(t', t)^* \right\rangle_{stoch} \right]. \tag{2.47}
\end{aligned}$$

Following closely the corresponding classical analysis, (see §IV of Ref. [4]), this may be approximated by adiabatic trajectories

$$\begin{aligned}
\hat{S}_{dyn}^{odd}(t) &= \frac{-1}{2} \int_0^t dt' \left\langle \hat{U}(t', t)^\dagger \hat{S}_{st}^0(t') \hat{U}(t', t) \right. \\
&\quad \left. - \hat{U}(t', t)^T \hat{S}_{st}^0(t')^* \hat{U}(t', t)^* \right\rangle_{stoch} \\
&\approx \frac{-1}{2} \int_t^{2t} dt' \left\langle \hat{U}(t', t)^\dagger \hat{S}_{st}^0(t') \hat{U}(t', t) \right. \\
&\quad \left. - \hat{U}(t', t)^T \hat{S}_{st}^0(t')^* \hat{U}(t', t)^* \right\rangle_{stoch} \\
&\approx \frac{-1}{2} \int_t^{2t} dt' \left\langle \hat{U}^0(t', t)^\dagger \hat{S}_{st}^0(t') \hat{U}^0(t', t) \right. \\
&\quad \left. - \hat{U}^0(t', t)^T \hat{S}_{st}^0(t')^* \hat{U}^0(t', t)^* \right\rangle_{stoch} \\
&= \frac{-1}{2} \int_0^t dt' \left\langle \hat{U}^0(t', t) \hat{S}_{st}^0(t') \hat{U}^0(t', t)^\dagger \right. \\
&\quad \left. - \hat{U}^0(t', t)^\dagger \hat{S}_{st}^0(t')^* \hat{U}^0(t', t) \right\rangle_{stoch}. \tag{2.48}
\end{aligned}$$

The second equality transforms from backward trajectories to future trajectories, and is justified because the evolution of the fluctuation in the dissipation is to a good approximation even in time. (The difference between the dissipations may be written as the difference of the difference between each dissipation and the average dissipation, which is the fluctuation.) The third equality is essentially Onsager's regression hypothesis:⁴² the future regression of a fluctuation is the same in an open system as in an adiabatic or isolated system. The fourth equality invokes the time reversibility of the adiabatic propagator. The adiabatic propagator is symmetric, $\hat{U}^0(t', t)^T = \hat{U}^0(t', t)$, and has the time symmetry $\hat{U}^0(t', t)^* = \hat{U}^0(2t - t', t)$. (For a mechanical non-equilibrium system, the Hamiltonian operator is extended into the future, $\hat{H}(t'; t) = \hat{H}(2t - t')$, $t' > t$, in order to preserve this symmetry. Of course the final equality refers only to $t' < t$ and so this is not needed explicitly.)

One can go further for two common cases. For a thermodynamic steady state system, the adiabatic rate of change of the static part of the reservoir entropy has

odd parity, $\hat{S}_{\text{st}}^0(t')^* = -\hat{S}_{\text{st}}^0(t')$. For a mechanical non-equilibrium system (time-dependent Hamiltonian operator) it has even parity, $\hat{S}_{\text{st}}^0(t')^* = \hat{S}_{\text{st}}^0(t')$. Accordingly, one can define

$$\hat{S}_{\text{dyn}}^{\text{odd};0}(t) \equiv \frac{-1}{2} \int_0^t dt' \left[\left\langle \hat{\mathcal{U}}^0(t', t)^\dagger \hat{S}_{\text{st}}^0(t') \hat{\mathcal{U}}^0(t', t) \right\rangle_{\text{stoch}} - \left\langle \hat{\mathcal{U}}^0(t', t)^T \hat{S}_{\text{st}}^0(t')^* \hat{\mathcal{U}}^0(t', t)^* \right\rangle_{\text{stoch}} \right] \quad (2.49)$$

With this and the above one sees that

$$\hat{S}_{\text{dyn}}^{\text{odd}}(t) \approx \pm \hat{S}_{\text{dyn}}^{\text{odd};0}(t), \quad (2.50)$$

with the positive sign for a steady state thermodynamic system, and the negative sign for a mechanical non-equilibrium system. Although this has no computational advantages over the preceding expression, and although it does not apply to a non-steady state thermodynamic system, it does have a certain aesthetic appeal for these two common cases.

With this or else the preceding expression, the entropy operator is in a form suitable for computation: because the expression invokes the adiabatic propagator, one does not have to compute the difficult stochastic, dissipative backward propagator.

III. EXECUTIVE SUMMARY

In this paper two results have been derived from first principles that lie at the foundations of non-

equilibrium quantum statistical mechanics. First, the non-equilibrium probability operator was obtained, Eq. (1.41). This was written as the exponential of an entropy operator, which in turn was shown to be the sum of a static and a dynamic part. The static part has the same form as the instantaneous equilibrium entropy operator, and the dynamic part is correction that accounts for the prior adiabatic changes that occur in non-equilibrium systems. The form of the probability operator is quite general, and it applies to mechanical non-equilibrium systems (i.e. time varying potentials), and to thermodynamic non-equilibrium systems (e.g. heat flow, hydrodynamic fluxes, chemical reactions).

Second, the stochastic, dissipative Schrödinger equation for an open non-equilibrium system was obtained, Eq. (2.34). Again the formulation is sufficiently general as to encompass both mechanical and thermodynamic systems. The time propagator was shown to comprise adiabatic, dissipative, and stochastic terms. The dissipative term was derived from the thermodynamic force and entropy fluctuation operators, which are in general non-linear operators. The variance of the stochastic operator was related to the dissipative operator by imposing the unitary condition on the propagator. This is the quantum version of the fluctuation-dissipation theorem. The non-equilibrium statistical average of an operator at a particular time was expressed in terms of the average density matrix generated by the stochastic, dissipative Schrödinger equation.

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- ¹ Attard, P. (2006), J. Chem. Phys. **124**, 224103.
 - ² Attard, P. (2009), J. Chem. Phys. **130**, 194113.
 - ³ Attard, P. (2012), *Non-Equilibrium Thermodynamics and Statistical Mechanics: Foundations and Applications*, (Oxford University Press, Oxford).
 - ⁴ Attard, P. (2014), arXiv:1405.1469.
 - ⁵ Attard, P. (2000), J. Stat. Phys. **100**, 445.
 - ⁶ Attard, P. (2002), *Thermodynamics and Statistical Mechanics: Equilibrium by Entropy Maximisation*, (Academic Press, London).
 - ⁷ Attard, P. (2013), arXiv:1401.1786.
 - ⁸ Attard, P. (2013), arXiv:1401.1787v3.
 - ⁹ Attard, P. (2014), arXiv:1404.2683.
 - ¹⁰ Messiah, A. (1961), *Quantum Mechanics*, (North-Holland, Amsterdam, Vols I and II).
 - ¹¹ Merzbacher, E. (1970), *Quantum Mechanics*, (Wiley, New York, 2nd edn).
 - ¹² Bogulbov, N. N. and Bogulbov, N. N. (1982), *Introduction to Quantum Statistical Mechanics*, (World Scientific, Singapore).
 - ¹³ Bialynicki-Birula, I. and Mycielski, J. (1976) Ann. Phys. (NY), **100**, 62.
 - ¹⁴ Weinberg S. (1989), Phys. Rev. Lett. , **62**, 485.
 - ¹⁵ Doebner, H.-D. and Goldin, G. A. (1992), Phys. Lett. A, **162**, 397.
 - ¹⁶ Doebner, H.-D. and Goldin, G. A. (1994), J. Phys. A: Math. Gen. **27**, 1771.
 - ¹⁷ Doebner, H.-D., Dobrev, V. K., and Nattermann, P., (1995), (editors), *Nonlinear, Deformed and Irreversible Quantum Systems*, (World Scientific, Singapore).
 - ¹⁸ Bugajski, S. (1991), Int. J. Theor. Phys. **30**, 961.
 - ¹⁹ Beretta, G. P., (1987), Foundations of Physics **17**, 365.
 - ²⁰ de Broglie, L. (1960), *Nonlinear Wavemechanics*, (Elsevier, Amsterdam).
 - ²¹ Laurent, B. and Roos, M. (1965), Nuovo Cimento **40**, 788.
 - ²² Shapiro, I. R. (1973), Sov. J. Nucl. Phys. **16**, 727.
 - ²³ Marinov, M. S. (1974), Sov. J. Nucl. Phys. **19**, 173.
 - ²⁴ Kupczynski, M. (1974), Lett. Nuovo Cimento **9**, 134.
 - ²⁵ Mielnik, B. (1974), Comm. Math. Phys. **37**, 221.
 - ²⁶ Pearle, P. (1976), Phys. Rev. D **13**, 857.
 - ²⁷ Shimony, A. (1979), Phys. Rev. A **20**, 394.
 - ²⁸ Kibble, T. W. B. (1978), Comm. Math. Phys. **64**, 73 (1978); **65**, 189 (1979).
 - ²⁹ Kibble, T. W. B. and Randjbar-Daemi, S. (1980), J. Phys. A **13**, 141.
 - ³⁰ Messer J. (1978), Lett. Math. Phys. **2**, 281.
 - ³¹ Moxnes, J. F. and Hausken, K. (2005), Annales de la Fondation Louis de Broglie, **30**, 309.

- ³² Lange H. (1985), *Nonlinear Analysis: Theory, Methods and Applications* **9**, 1115.
- ³³ Garashchuk, S., Dixit, V., Gu, B., and Mazzuca, J., (2013), *J. Chem. Phys.* **138**:054107.
- ³⁴ Kostin, M. D. (1972), *J. Chem. Phys.* **57**, 2589.
- ³⁵ Doebner, H.-D., Goldin, G.A., and Nattermann, P. (1999), *J. Math. Phys.* **40**, 49.
- ³⁶ Weiss, U. (1993), *Quantum Dissipative Systems*, (World Scientific, Singapore).
- ³⁷ Dekker, H. (1981), *Phys. Rep.* **80**, 1.
- ³⁸ Schuch, D. (2012), *J. Phys. Conf. Ser.* **380**, 012009
- ³⁹ Attard, P. (2005), *J. Chem. Phys.* **122**, 154101.
- ⁴⁰ Attard, P. (2004), *J. Chem. Phys.* **121**, 7076.
- ⁴¹ Attard, P. (2005), *J. Chem. Phys.* **122**, 244105.
- ⁴² Onsager, L. (1931) *Phys. Rev.* **37**, 405.
- ⁴³ Green, M. S. (1954), *J. Chem. Phys.* **22**, 398.
- ⁴⁴ Kubo, R. (1966), *Rep. Progr. Phys.* **29**, 255.
- ⁴⁵ Attard, P. and Gray-Weale, A. (2008), *J. Chem. Phys.* **128**, 114509.
- ⁴⁶ Attard, P. (2009), *Phys. Rev. E* **80**, 041126.